Thermoelectric Properties of Wires Bi_2Te_3 in the Glass Coating p and n Type

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Abstract — **The aim of our research was to prepare micro- and nanowires of n- and p-type Bi_2Te_3 in glass insulation and to study their thermoelectric properties as a function of heat treatment, i.e., annealing, recrystallization, and wire diameter. The n- and p-type Bi_2Te_3 wires in glass insulation were prepared via liquid-phase casting through heating a glass tube containing the Bi_2Te_3 material of the appropriate composition using an outer furnace. For the first time, by re-drawing wires vitrified Bi_2Te_3 were obtained with the wires diameter up to 1 mkm. Due to the fact that the resistivity of the thin wires (d = 2 mkm) is almost an order of magnitude smaller than in the wires of p-type Bi_2Te_3 (d> 50 mkm), Power factor= $\alpha^2\sigma$ at 300 K = 3,5*10^{-5} W/cm*K^2 exceeds the maximum P.f= 1,2*10^{-5} W/cm*K^2, obtained in wires with d> 50 mkm, even after additional annealing for 24 hours.It has been shown that the isothermal annealing increases both thermopower α and resistivity ρ in the samples of hole conductivity; unlike p-type, the parameters α and ρ vary only slightly after annealing. The parameters of the annealed samples hardly changed during the entire test period. Therefore, it is recommended to subject Bi_2Te_3 wires in glass insulation to an additional long-term annealing at appropriate temperatures in the case of their use in thermoelectric energy converters.**

Index Terms — **Bi_2Te_3 microwires, annealing, Power factor.**

INTRODUCTION

It is known that bismuth tellurides and selenides are among the best thermoelectric materials at 300< T< 600 K.

A significant progress in the design of thermoelectric generators and coolers is based on these materials of n- and p-type [1-5].

There are quite a number of patents, review articles, and world-class publications [1-10]; however, the growth rates in the efficiency of thermoelectric energy converters are not great.

In recent years, along with traditional thermoelectric materials, new materials based on completely new principles have been studied [6-10].

The figure of merit Z of a thermoelectric material is defined by the expression

$$Z = \frac{\alpha^2\sigma}{\chi}, \chi=\chi_p + \chi_1, \qquad (1)$$

where χ_p is the phonon thermal conductivity of the lattice and χ_1 is the thermal conductivity of an electronic system. An increase in the figure of merit of the material leads to an increase in the efficiency of energy-conversion thermoelectric element.

At present, low-dimensional structures hold a particular position. The figure of merit of a thermoelectric material depends on the ratio of mobility μ to the phonon component of thermal conductivity χ_p, which decreases in low-dimensional structures because of additional surface scattering.

A difference in the de Broglie wavelength of phonons and electrons can lead a significant decrease in the phonon thermal conductivity in comparison with the mobility. The result is that the figure of merit of the material can increase.

Another aspect is that the family of materials of bismuth telluride (Bi_2Te_3) exhibits the properties of a topological insulator (TI) with a large energy gap and the surface states consisting of a single Dirac cone [13].

TIs are materials with a gap of an insulator, which exhibit dependences similar to quantum Hall in the absence of a magnetic field [14-16].

It is assumed that TIs can be used to design quantum computers, because they contain surface states which are topologically protected by the surface.

Superlattices based on Bi_2Te_3 and Sb_2Te_3 were studied in [10].

For the structure of Bi_2Te_3 and Sb_2Te_3 of the p-type conductivity, values of Z = (7-8) * 10^{-3} K^{-1} are obtained at T = 200-300 K.

In [11, 12], nanowires of semiconductor $A^{II}B^{VI}$ compounds are theoretically studied: CdTe, ZnTe, ZnSe, and ZnS. Calculations show the possibility to obtain ZT = 6.

The aim of our research was to prepare micro- and nanowires of n- and p-type Bi_2Te_3 in glass insulation and to study their thermoelectric properties as a function of heat treatment, i.e., annealing, recrystallization, and wire diameter.

Single-crystal films and nanowires of Bi_2Te_3 with a thickness of a few nanometers are exceptionally promising materials both for the observation and study of unique physical properties and for potential practical applications.

I. EXPERIMENT

The n- and p-type Bi_2Te_3 wires in glass insulation were prepared via liquid-phase casting through heating a glass tube containing the Bi_2Te_3 material of the appropriate composition using an outer furnace.

The measurements of electric and thermoelectric properties were carried out by a standard technique for samples with a length of 5-7 mm cleaved from different parts along the length of the microwire (MW).

The study of the dependences of physical parameters on process conditions for MWs showed that the thermoelectric coefficient α for the samples of the hole p- or electron n-conductivity at 300 K are in the range: $\boldsymbol{\alpha_p}$ = +(150÷300) μV/K; $\boldsymbol{\alpha_n}$ = -(100÷140) μV/K; $\boldsymbol{\rho_p}$ = (1÷7)*10^{-3} Ω*cm; $\boldsymbol{\rho_n}$ = (1÷3)*10^{-3} Ω*cm, respectively [13].

To stabilize the parameters of the MWs, we carried out isothermal annealing at different temperatures and for different times. The results are shown in Figs. 1- 4.

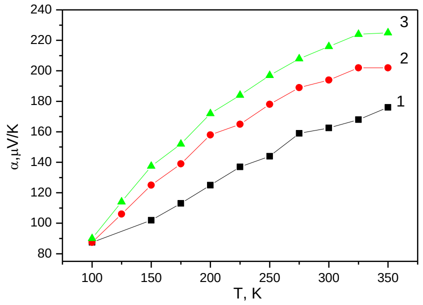

Fig. 1. Temperature dependence of the thermopower of the p-type Bi_2Te_3 wires: (1) before annealing, (2, 3) after annealing at 473 K. The annealing time is (2) 1 h and (3) 24 h.

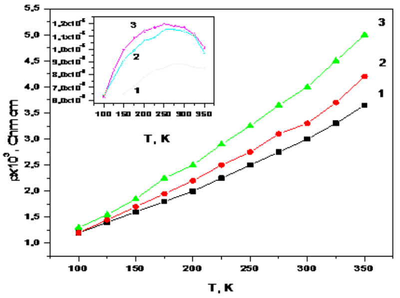

Fig. 2. Temperature dependence of the resistivity of the p-type Bi_2Te_3 wires: (1) before annealing, (2, 3) after annealing at 473 K. Inset: Power factor of the p-type Bi_2Te_3 wires: (1) before annealing, (2, 3) after annealing at 473 K. The annealing time is (2) 1 h and (3) 24 h.

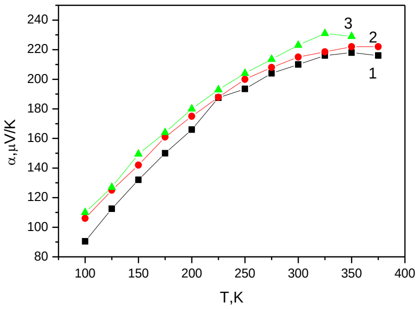

Fig. 3. Temperature dependence of the thermoelectric power of n-type Bi_2Te_3 wires annealed at 450 K. The annealing time is (1) 48 h, (2) 96 h, and (3) 73 h.

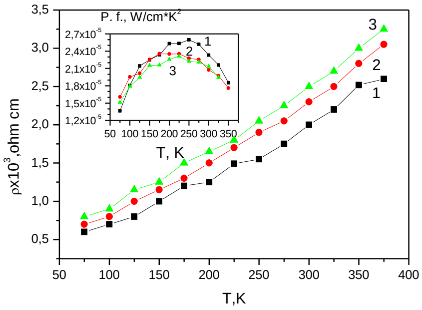

Fig. 4. Temperature dependence of the resistivity of n-type Bi_2Te_3 wires annealed at 450 K. The annealing time is (1) 1 h, (2) 72 h, and (3) 96 h. Inset: Power factor of n-type Bi_2Te_3 wires annealed at 450 K.

These figures show that the isothermal annealing increases both thermopower α and resistivity ρ in the samples of hole conductivity; the higher the temperature and annealing time, the higher α and ρ at T = 300 K.

The results for the n-type samples are shown in Figs. 3 and 4. It is evident from the figures that, unlike p-type, the parameters α and ρ vary only slightly after annealing.

According to formula (1), the expression for thermoelectric efficiency contains the quantity $\alpha^2\sigma$, which is called Power factor (P.f.). The calculation of P.f according to Figs. 1- 4 is shown in Figs. 2 and 4 (inset). The maximum value of P.f. for p-type is 1.2*10^{-5} W/cm*K^2, while for n-type P.f.= 2.5 * 10^{-5} W/cm*K^2 in a temperature range of 200-300 K.

If we take the thermal conductivity of Bi_2Te_3 wires, as in bulk materials, χ= 1.4*10^{-2} W/cm*K^2, then the maximum value of ZT after annealing in a temperature range of 250-300 K is 0.27 for the n-type wires and 0.56 for the p-type Bi_2Te_3 samples.

Taking into account the remarkable manufacturability, reliable protection from the environment owing to the glass insulation, and almost nonwaste production of the wires, they are undoubtedly regarded promising for using in thermoelectric energy converters.

Bi_2Te_3 wires of n- and p-type were subjected to aging tests, because the stability over time of the parameters is a necessary condition for using them as elements of thermoelectric energy converters.

The samples (Bi_2Te_3 wires of n- and p-type in glass insulation) were subjected to isothermal annealing at 370 K for 60 h. After that, the samples were held at T = 300 K for a month, and the thermoelectric parameters α and ρ were measured at T = 300-77 K.

After the measurement of the parameters, the samples were subjected to a repeated thermal annealing at 100°C for 40 h and subsequently stored at room temperature for 2 months. The results of measurements show that the parameters α and ρ of unannealed MWs change.

The parameters of the annealed samples hardly changed during the entire test period.

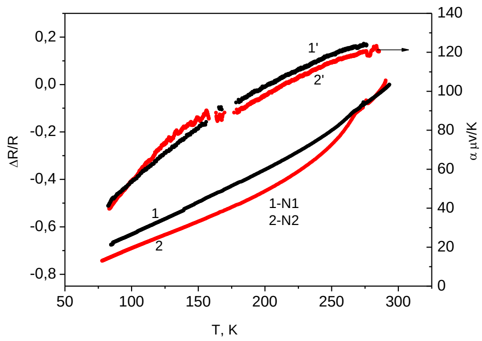

Fig. 5. Temperature dependences of the resistance (1, 2) and thermopower (1’, 2’) Bi_2Te_3 wires, 1. d= 8 mkm, 2. d= 2 mkm.

For the first time, by re-drawing wires vitrified Bi_2Te_3 were obtained with the wires diameter up to 1 mkm. It was found that the resistivity ρ at 300 K, the p-type wires Bi_2Te_3 with diameters 8 mkm and 2 mkm are ρ=0.8*10^{-3} Om*cm and 0,5*10^{-3} Om*cm respectively, significantly less than in the initial p-type wires, obtained by casting from the liquid phase. With decreasing temperature from 300 K to 77 K, the resistivity decreases by 70-75%, as in the wires with d> 50 mkm (Fig. 5, curver 1, 2).

Fig. 5, curve 1’, 2’ shows the temperature dependence of the thermopower α (T) wires of the two diameters in the range 77-300 K. The maximum value at 300 K is +125 µV / K, which is significantly less than in the wires with d > 50 mkm.

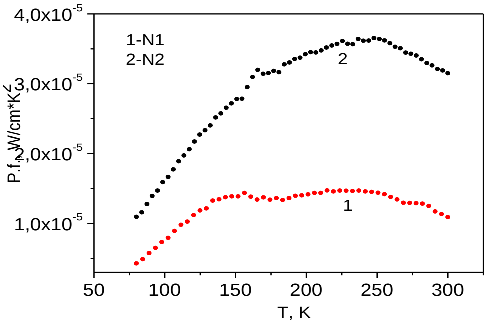

Fig. 6. Temperature dependences of the thermoelectric Power factor p- type Bi_2Te_3 MWs. 1. d= 8 mkm, 2. d= 2 mkm.

However, due to the fact that the resistivity of the thin wires (d = 2 mkm) is almost an order of magnitude smaller than in the wires of p-type Bi_2Te_3 (d > 50 mkm), Power factor= $\alpha^2\sigma$ at 300 K = 3,5*10^{-5} W/cm*K^2 (Fig. 6, a,b) exceeds the maximum P.f. = 1,2*10^{-5} W/cm*K^2, obtained in wires with d> 50 mkm, even after additional annealing for 24 hours.

Therefore, it is recommended to subject Bi_2Te_3 wires in glass insulation to an additional long-term annealing at appropriate temperatures in the case of their use in thermoelectric energy converters.

Thin Bi_2Te_3 -wires are more perspective, but demand additional researches on stability of thermoelectric characteristics.

II. CONCLUSION

Temperature dependences of resistance R(T) and thermopower a(T) Bi_2Te_3 n-type in a glass cover prepared by liquid phase have been investigated in temperature range 77-300 K.

For the first time, by re-drawing wires vitrified Bi_2Te_3 were prepared wires with the diameter up to 1 mkm. It was found that the resistivity ρ at 300 K, the p-type wires Bi_2Te_3 with diameters 8 mkm and 2 mkm are ρ=0.8*10^{-3} Om*cm and 0,5*10^{-3} Om*cm respectively, significantly less than in the initial p-type wires (d> 30 mkm). Due this fact, P.f. in thin wires exceeds P.f. in wires with d> 50 mkm even after additional annealing for 24 hours. The parameters of the annealed samples hardly changed during the entire test period.

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