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Single-Crystal Layers of p- and n-Type Bismuth Telluride Topological Insulators for Micro-Cooling Devices

The paper presents the results of experimental studies of the thermoelectric properties and oscillation effects (Shubnikov-de Haas oscillations) of single-crystal layers of bismuth telluride topological insulators of p- and n-type without substrates, with thicknesses of 17 μm and 20 μm, respectively, obtained by mechanical exfoliation of layers from a single-crystal ingot of the corresponding composition using a technique developed by the authors of the article. Cyclotron masses and charge carrier quantum mobilities characteristic of surface states of topological insulators were estimated using experimental data on Shubnikov-de Haas oscillations in longitudinal (B||I) and transverse (B⊥I) magnetic fields up to 14 T. The force factor was calculated in the temperature range of 2–300 K from the temperature dependences of resistance and thermoelectric power. It was established that the maximum value of the power factor $\alpha^2\sigma$ *was observed in the temperature range of 100–250 K and corresponds to the best maximum values available in the literature for perfect single crystals. Based on the obtained layers of* Bi_2Te_3 *p-type and n-type foil – Bi-17 at%, a design was created – a micro-cooling device that allows obtaining* $\Delta T = 12^o$ *on the area of 0.01* cm^2*, which is an important factor for the development of new highly efficient thermoelectric materials based on thinner layers for their practical use in micro-coolers.*

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Keywords: thermoelectric materials, topological insulators, layers, foil, single-crystal layers, Bi_2Te_3, Shubnikov-de Haas oscillations, charge carrier mobilities, cooling device.

Introduction

Thermoelectric materials that convert thermal energy into electrical energy and vice versa have become the object of increased attention due to intense development of alternative energy [1–3]. Thermoelectric materials based on solid solutions of bismuth and antimony chalcogenides are widely used in the range of temperatures close to room temperature in various cooling devices [4, 5].

The efficiency of both generating and cooling thermoelectric devices depends on the dimensionless thermoelectric efficiency of material $ZT = \alpha^2\ T/(\chi_e + \chi_l) \sim 1$, where α, σ, χ, and T are the Seebeck coefficient (thermopower), σ is the electrical conductivity of the material, χ is the thermal conductivity of the material, and T is the absolute temperature. Increasing the *ZT* parameter of thermoelectric materials in the operating temperature range has been one of the most important tasks over the past decades.

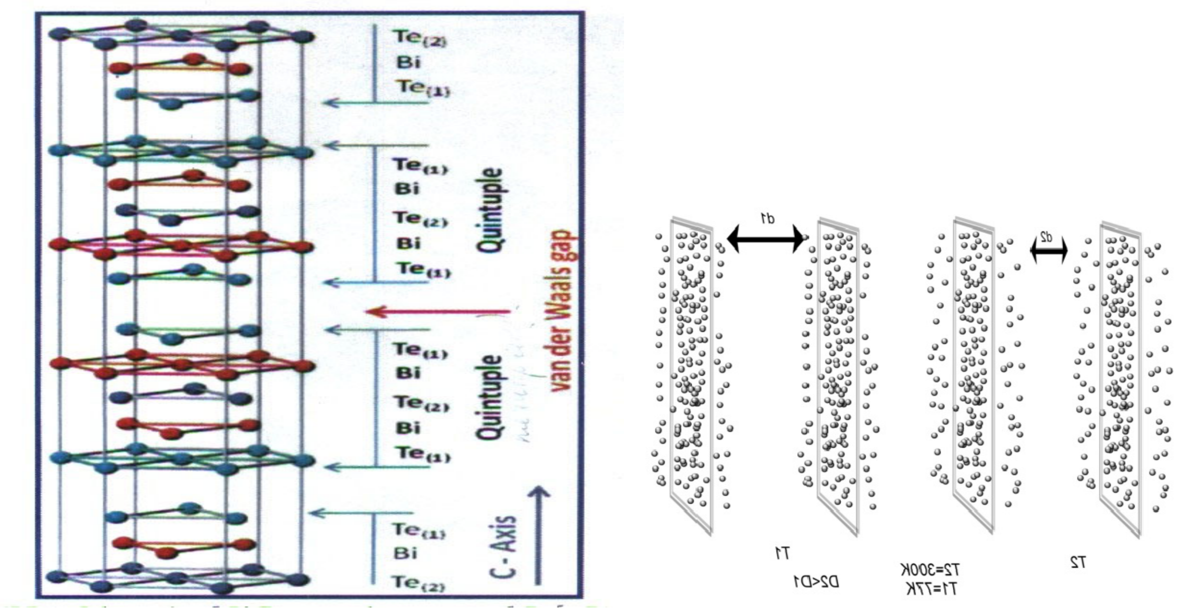
In recent years, much attention has been paid to the development of new concepts – low-dimensional structures [6,8] and topological insulators [9, 10]. Theoretical calculations and experimental results demonstrate that in size-limited structures, thermoelectric efficiency can be effectively increased due to the manifestation of the quantum size effect and an increase in phonon scattering. In topological insulators, a significant modification of the phonon spectrum occurs, and thermoelectric properties depend significantly on the composition, structure, and dimensions of the objects under study.

The purpose of this work was to obtain p- and n-type single-crystal layers without substrates based on bismuth telluride Bi_2Te_3, study the Shubnikov-de Haas (SdH) oscillations, calculate the cyclotron masses and charge carrier mobilities, investigate the thermoelectric properties, and evaluate the thermoelectric efficiency in the temperature range of 4.2–300 K. A miniature cooling device operating at 300 K was created using the materials studied.

1. Samples and technology for manufacturing n and p-type single-crystal layers of Bi_2Te_3 without substrates

It is known that semiconductors such as bismuth telluride (selenide) and antimony telluride are layered crystals of a rhombohedral structure with C2 and C3 symmetry axes. A hexagonal unit cell is most often used to describe the crystal structure. The crystal lattice is formed by periodically ordered layers lying in a plane perpendicular to the C3 symmetry axis (Fig. 1 *a*). As shown in Fig. 1 *a*, each layer consists of five atomic planes (quintets) in the following sequence: Te1–Bi–Te2–Bi–Te1, where Te1 and Te2 denote tellurium atoms in different positions. If we consider an individual layer, the atoms within it are identical and arranged to form a flat hexagonal lattice.

Chemical bond within quintets is known to be covalent-ionic. The quintets are relatively far apart and weakly bonded by van der Waals forces, which determines the anisotropy of the single crystal properties. Mechanical exfoliation occurs as a result of the breakdown of weak van der Waals bonds between Te(1) and Te(1) and the formation of several pentaatomic planes.



a *b*

Fig. 1. (a): Schematic representation of Bi_2Te_3 crystal structure D3d5-R(-3)m is space group showing quintuple layers and van der Waals gap localization, Te(1)-Te(1) is weak bond and Bi-Te(1) is strong bond. (b): schematic representation of two adjacent Te(1)-Te(1) atomic layers at T = 300 K (1) and 77 K(2)

It was the weak bond that allowed us to obtain single-crystal layers with thicknesses of 5–20 μm both on scotch tape substrates and without substrates (patents 11.12) by mechanical exfoliation from a single-crystal ingot of the corresponding composition (Fig. 2. *a*). The initial bulk single-crystal samples of the corresponding composition were grown by the Bridgman method (Fig. 2. *a*) and were high-quality single-crystal ingots, which was confirmed by studies of photoemission spectroscopy with high angular resolution.

a *b* *c*

Fig. 2. a – a bulk single-crystal Bi_2Te_3 ingot and blanks cut from it for exfoliation, b – layers without substrates on a water surface (according to patent 12), c – layers without substrates transferred onto graph paper

X-ray diffraction studies revealed that the layers (with a thickness of d = 5–20 μm) exfoliated from a single-crystal ingot are single crystals with the C_3 axis perpendicular to the plane of the layers. A two-probe method was used to measure the thermoelectric power in the temperature range of 2.1 K–300 K, and a four-probe method was used to study the resistance, magnetoresistance, and Shubnikov-de Haas oscillations in the temperature range of 2.1 K–4.2 K and magnetic fields up to 14 T.

A special rotating device made it possible to rotate the sample in a magnetic field B (up to 14 T) in different planes at temperatures of 2K–300K and to measure the transverse and longitudinal magnetoresistance, their anisotropy and Shubnikov-de Haas oscillations, to calculate the cyclotron masses and mobilities of charge carriers.

2. Results and discussion

The rotation diagrams of the transverse magnetoresistance R(O) and thermoelectric power S(0) of single-crystal Bi_2Te_3 layers of p- and n-type with thicknesses of 17 μm and 20 μm, respectively, at temperatures of 4.2 K and 300 K and magnetic fields up to 14 T, as well as the field dependences of the transverse ($B\perp I$) and longitudinal ($B||I$) magnetoresistance at temperatures of 1.5 K – 300 K were studied. The thermopower anisotropy α (0) is rather low: = 1.25–1.5. Fig. 3 shows the experimental field dependences of the relative R_B/R_0 (B) of the longitudinal (1) and transverse (2) magnetoresistance in magnetic fields up to 14 T of the Bi_2Te_3-p layer, d = 17 μm at 4.2 K.

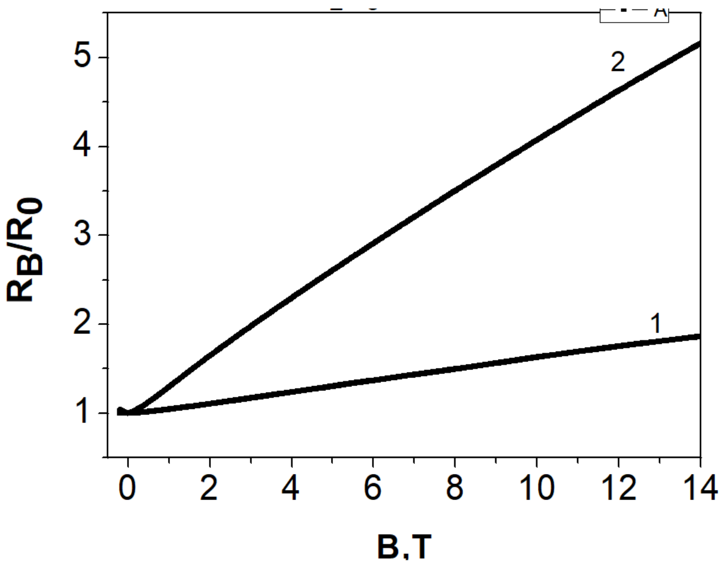
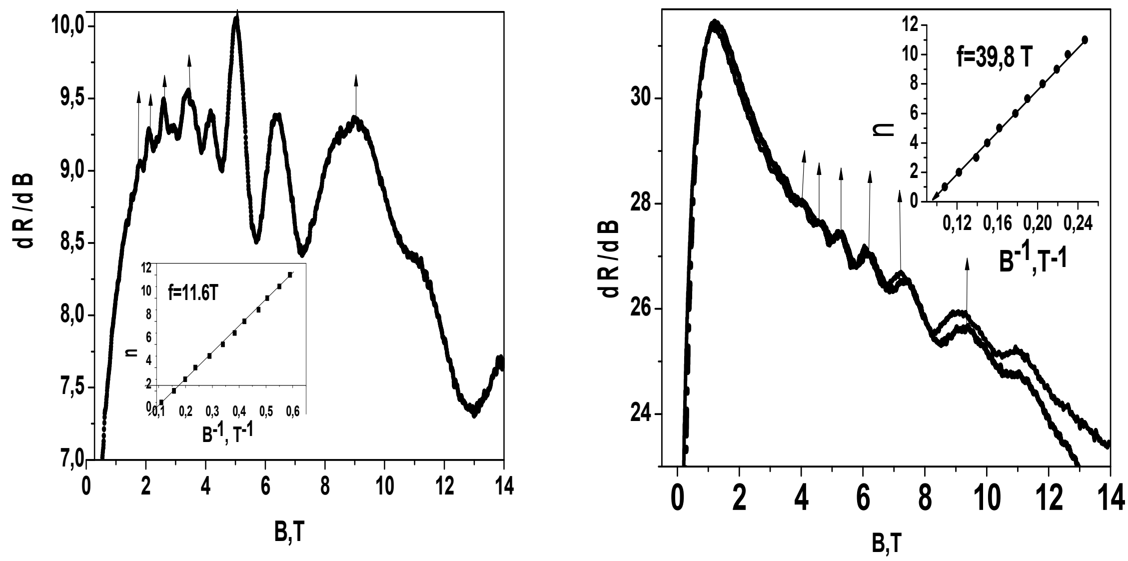


Fig. 3. Field dependences of the presented longitudinal (1) and transverse (2) magnetoresistance R_B/R_0 (B) of the Bi_2Te_3-p type layers, d = 17 μm at 4.2K

The anisotropy of resistance and magnetoresistance ***A*** at low temperatures is quite large even in magnetic fields of 14 T. $A = (R\backslash/R//)$ = 5.

Figs 4 and 5 show the experimental field dependences of the derivatives of the longitudinal and transverse magnetoresistance dR/dB(B) at temperatures of 4.2 K and 2.1 K for p-type and n-type layers, respectively.

For p-type layers, the frequency of SdH oscillations, proportional to the cross-section of the Fermi surface, is $f_1 = \Delta^{-1} = 11.6$ T for longitudinal and $f_2 = \Delta^{-1} = 39$ T for transverse magnetoresistance.



a *b*

Fig. 4. Field dependences of the derivatives of the longitudinal (a) and transverse (b) magnetoresistances $\partial R/\partial B(B)$ at 4.2K and 2.1K of Bi_2Te_3 p-layers, d = 17μm
Inside – dependences of the quantum number n of the SdH oscillations on B^{-1}

It was found that at $B||I$, the transition to the ultra-quantum region of magnetic fields (doubling the period of SdH oscillations) occurs in a magnetic field of B_{uqt} = 2–3 T for longitudinal magnetoresistance and B_{uqt} = 2–3 T = 9 T for transverse magnetoresistance and indicates spin damping of the first harmonic of SdH oscillations. The experimental value of the phase shift of the Landau level index was determined from the linear dependence of the quantum number $n(B^{-1}) = 0$ by extrapolating the dependence of the index n on the inverse magnetic field $n(B^{-1})$ (insets in Fig. 4 (*a*, *c*). It was found that the phase shift is 0.5 for both longitudinal and transverse magnetoresistance, which is typical for topological insulators.

Magnetoresistance in transverse ($B\perp I$) and longitudinal ($B||I$) magnetic fields up to 14 T was investigated in single-crystal layers of n-type Bi_2Te_3 in the temperature range of 1.5–300 K. Experimental field dependences of the reduced magnetoresistance $\Delta R/R(B)$ at 4.2 K and 2.1 K are shown in Fig. 5.

Data obtained from the Shubnikov-de Haas (SdH) effect were used to calculate the cyclotron effective masses and charge carrier quantum mobilities. It is known that the frequency of quantum oscillations of magnetoresistance, f, according to the Lifshitz-Onzeiger relations, is proportional to the cross-sectional area of the Fermi surface, $S(k_F)$.

$$f = \Delta(\mathrm{B}) = \left(\frac{\hbar}{2\pi e}\right) S(k_F),$$

where k is the electron wave vector, $\hbar$ is the reduced Planck constant.

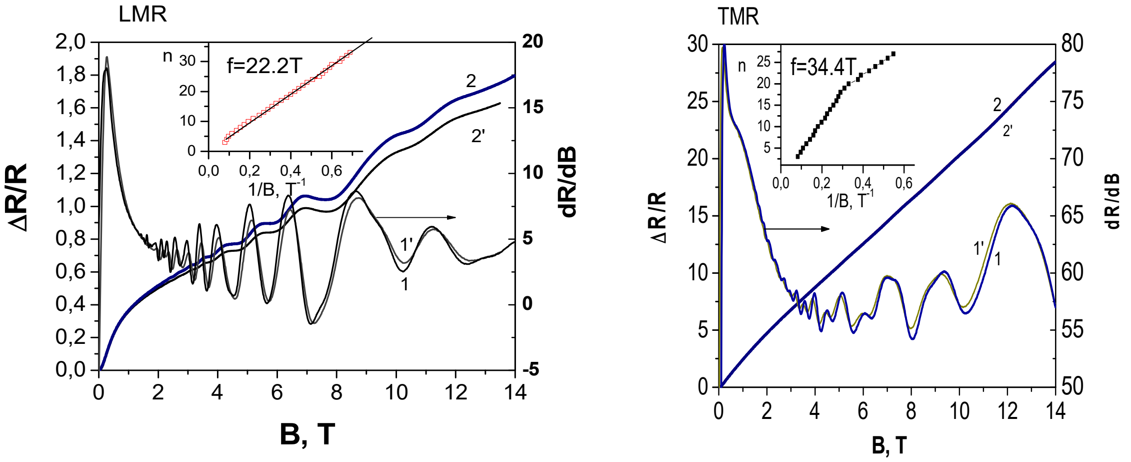


Fig. 5. Field dependences of the reduced transverse magnetoresistance ΔR/R(B) (1) and derivative ∂R/∂B(B) (2) at temperatures of 2.1 K (1, 2) and 4.2 K (1', 2') of the Bi_2Te_3 layer, d = 20 μm. Inset: dependence of the quantum number n of the SdH oscillations on the inverse magnetic field B^{-1}

The temperature dependences of the amplitude of the SdH oscillations made it possible to calculate the effective cyclotron masses m_c at $B||I$ and at $B\perp I$.

The ratio of amplitudes $A(T_1, B_n)$ and $A(T_2, B_{n2})$ is:

$$\frac{A(T_1,B_n)}{A(T_2,B_n)} = \frac{T_1}{T_2}\cdot\frac{sh\left(\frac{2\pi^2 m^* ckT_2}{|e|\hbar B_n}\right)}{sh\left(\frac{2\pi^2 m^* ckT_1}{|e|\hbar B_n}\right)} \quad (1)$$

This expression is valid if the Dingle temperature $T_D = \pi h/n\tau k$, which characterizes the broadening of the Landau levels as a result of carrier scattering, remains constant in the temperature range from T_1 to T_2.

At low temperatures, the relaxation time τ is determined by impurities and imperfections of the crystal lattice and is practically independent of T, i.e., in the region of residual resistance, at $T \leq 4.2$ K. In our experiment, this condition was met.

In the case when $T_1 = 1/2T_2$, the expression for the cyclotron effective mass m^* has the form:

$$m^* = \frac{|e|\hbar B_n}{4\pi^2 m^* ckT_1} Arch\left[\frac{A(T_1,B_n)}{A(T_2,B_n)}\right] \quad (2)$$

The cyclotron masses calculated according to expression (2) from the $\partial R/\partial B(B)$ dependences at temperatures of 4.2 K and 2.1 K (Fig. 2, 3) were m_C^2 =0.11m_0 for longitudinal magnetoresistance and $m_C^2 = 0.13$ m_0 for transverse ($B\perp I$), which is in good agreement with the data obtained on bulk samples and films of Bi_2Te_3, Bi_2Se_3 from SdH oscillations.

The Dingle temperature T_D, which characterizes the broadening of the Landau levels as a result of carrier scattering, equivalent to an increase in temperature by the value T_D, was determined from the ratio of the amplitudes of the SdH oscillations at two successive values of the magnetic fields B_n and B_{n+1}.

The values were calculated for 5–6 points (maxima) on the SdH oscillations and the average value was determined.

The ratio of the amplitudes is:

$$\frac{A(T, \mathrm{B}_n)}{A(T, \mathrm{B}_{n+1})} = \left(\frac{\mathrm{B}_{n+1}}{\mathrm{B}_n}\right)^{\frac{1}{2}} \frac{sh\left(\frac{2\pi^2 m^* ckT}{|e|\hbar \mathrm{B}_{n+1}}\right)}{sh\left(\frac{2\pi^2 m^* ckT}{|e|\hbar \mathrm{B}_n}\right)} \times exp\left[\frac{2\pi^2 m^* ckT_D}{|e|\hbar}\right]\left(\frac{1}{\mathrm{B}_{n+1}} - \frac{1}{\mathrm{B}_n}\right)$$

Where T_D was found by taking the logarithm. From the SdH oscillations on the longitudinal magnetoresistance, the calculated Dingle temperature was T_D = 1.3 K, and on the transverse one T_D = 6 K.

Considering that the Dingle temperature $T_D = \frac{\hbar}{\pi k_B} \cdot \frac{1}{\tau}$, where τ is the relaxation time, the charge carrier mobility (quantum mobility) was determined from the relation:

$$\mu_S = \frac{\hbar e}{2\pi k_B} \cdot \frac{1}{m_e T_D}$$

and was for longitudinal magnetoresistance μ = 12.09*10^3 cm^2/V*sec and for transverse $\mu^{\perp}$=2.32*10^3 cm^2/V*sec, which coincides with the values obtained from the Hall effect for n-type Bi_2Te_3 films at $B \perp I$ and significantly exceeds the values for longitudinal magnetoresistance $B \perp I$.

For *p*-layers, the cyclotron mass, calculated according to expression (2) from the ∂R/∂B(B) dependences for transverse magnetoresistance, was $m_C^2 = 0.1\, m_0$. And the edge mobilities were μ = 14.1*10^3 cm^2/V*sec.

The temperature dependences of the resistivity ρ(T) and thermoelectric power α(*T*) of p-type Bi_2Te_3 layers with *d* = 17 μm and *n*-type with *d* = 20 μm were studied, on the basis of which the temperature dependence of the power factor $\alpha^2\sigma(T)$ was calculated.

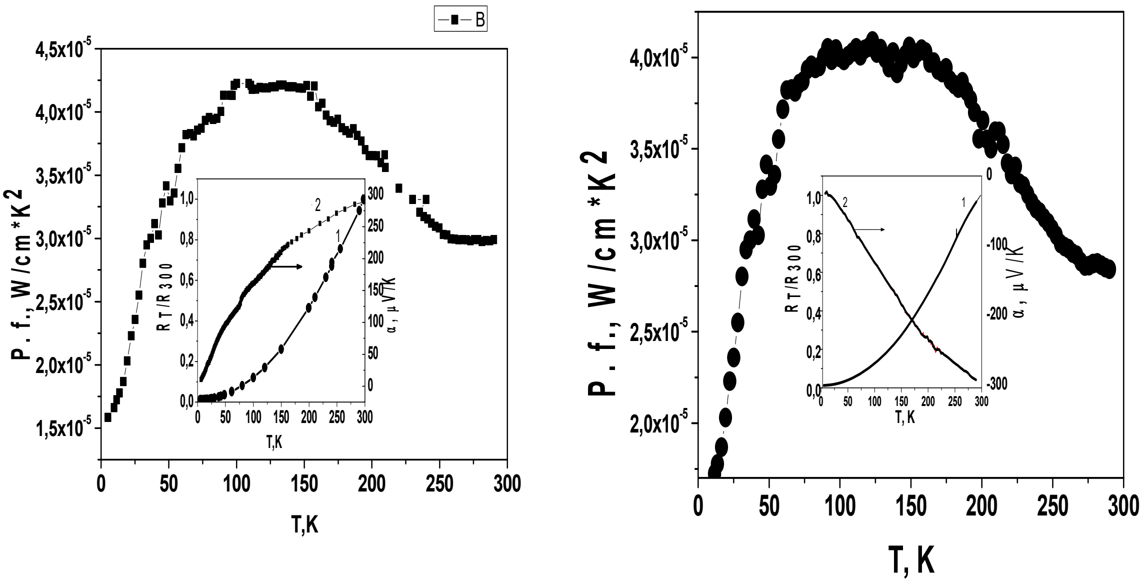


Fig. 6. Temperature dependences of the force factor $\alpha^2\sigma(T)$ of the Bi_2Te_3 layer, n-type d = 20 μm (a) and p-type d = 17 μm (b). Inset: temperature dependences of the relative resistance $R_T / R_{300}(T)$ (curve 1) and thermoelectric power α (T) (curve 2 – scale on the right)

The temperature dependences of the power parameter P.f. = $\alpha^2\sigma$ were determined from the data of thermopower and resistivity. The maximum value of P.f. is $4.3*10^{-5}$ W/*cm*K^2 in a wide temperature range of 75 K–200 K. At 300 K P.f. = $3.2*10^{-5}$ W/*cm*K^2. Using data on the thermoelectric efficiency of p- and n-type Bi_2Te_3 layers, as well as our previously obtained results on the thermoelectric efficiency of n-type foils with the composition Bi-17% Sb [13], the dependence of the cooling effect (temperature gradient on the passing current ΔT(I) through a structure in the form of thermocouples from n- and p-layers at 300 K was investigated.

Fig. 7 shows the dependence of the temperature gradient ΔT on the direct current passing through various n-p structures at 300 K.

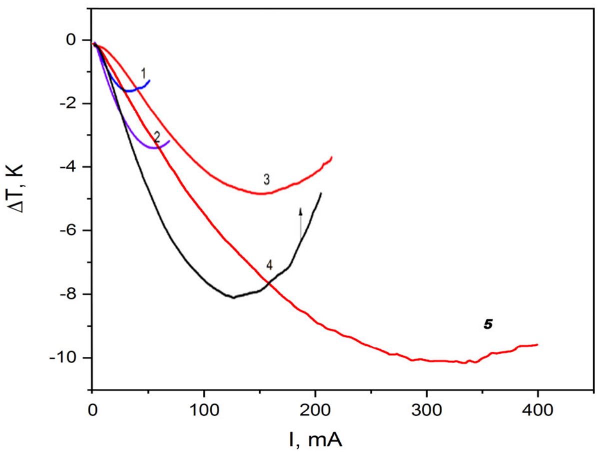


Fig. 7. Temperature gradient ΔT as a function of current passing through: (curve 1) – one thermocouple made of n- and 1 p-Bi_2Te_3 layers 20 µm thick on scotch tape substrates, (curve 2) – two segmented n- and p-type Bi_2Te_3 thermocouples on substrates, (curve 3) – a thermocouple made of 1 n-type Bi_2Te_3 layer without substrate and 1 p-type Bi_2Te_3 layer without substrate, (curve 4) – a thermocouple made of 1 p-type Bi_2Te_3 layer without substrate and 1 n-type $Bi_{0.84}$–Sb_{16} foil 20 µm thick, (curve 5) – a thermocouple made of two parallel-connected p-type Bi_2Te_3 layers without substrates and 1 n-type $Bi_{0.84}$–Sb_{16} foil 20 microns thick.

Thus, the device under study made it possible to obtain a temperature difference of $\Delta T = 12^{\circ}$ over an area of 0.01 cm^2 at 300 K (Fig. 7).

Conclusions

Using the mechanical cleavage method, single-crystal layers of the n- and p-type topological insulator Bi_2Te_3 were obtained, with a layer thickness of 10–20 µm without substrates.

The SdH oscillation frequency was calculated from the SdH oscillations, and the cyclotron masses, Dingle temperature, and charge carrier mobilities for two magnetic field directions were estimated. It was shown that the charge carrier quantum mobilities at 4.2 K for $H||I$ exceed the values obtained for bulk samples and films of the corresponding composition.

It was found that the phase shift of the Landau level index is 0.5 in both parallel and perpendicular magnetic fields, which confirms the presence of surface states of the layers of topological insulators Bi_2Te_3.

The calculated values of the temperature dependence of the force factor have a wide maximum in the temperature range of 75–200 K, in the region of 300 K.

Using the data on the thermoelectric efficiency of p-type Bi_2Te_3 layers with a thickness of 17 μm and the results we obtained earlier on Bi-17 at % Sb foil (n-type, 20 μm thick), a miniature micro-cooling device was designed and investigated in the form of a thermocouple made of p-type Bi_2Te_3 layers and n-type Bi-17 at % Sb foil, which makes it possible to obtain a temperature difference of $\Delta T = 12^{o}$ on an area of 0.01 cm^2 at 300 K, which is an important factor and opens up ways to increase the thermoelectric efficiency and thermo-cooling effect at 300 K.

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Монокристалічні шари топологічних ізоляторів на основі телуриду вісмуту p- та n-типу для мікроохолоджуючих пристроїв

У статті представлені результати експериментальних досліджень термоелектричних властивостей та коливальних ефектів (коливань Шубнікова-де Гааза) монокристалічних шарів топологічних ізоляторів телуриду вісмуту p- і n-типу без підкладок, товщиною 17 мкм та 20 мкм відповідно, отриманих шляхом механічного відшаровування шарів з монокристалічного злитка відповідного складу за методикою, розробленою авторами статті. Циклотронні маси та квантові рухливості носіїв заряду, характерні для поверхневих станів топологічних ізоляторів, були оцінені з використанням експериментальних даних про коливання Шубнікова-де Гааза в повздовжніх (B||I) та поперечних (B⊥I) магнітних полях до

14 Тл. Коефіцієнт сили був розрахований в діапазоні температур 2–300 K за температурними залежностями опору та термоерс. Встановлено, що максимальне значення коефіцієнта потужності спостерігається в діапазоні температур 100–250 K і відповідає найкращим максимальним значенням, доступним в літературі для ідеальних монокристалів. На основі отриманих шарів фольги Bi_2Te_3 p-типу і n-типу – Bi-17 ат%, було створено конструкцію – мікроохолоджувальний пристрій, який дозволяє отримати $\Delta T = 12^o$ на площі 0.01 $см^2$, що є важливим фактором для розробки нових високоефективних термоелектричних матеріалів на основі тонших шарів для їх практичного використання в мікроохолоджувачах.

Ключові слова: термоелектричні матеріали, топологічні ізолятори, шари, фольга, монокристалічні шари, Bi_2Te_3, коливання Шубнікова-де Гааза, рухливість носіїв заряду, охолоджувальний пристрій.

Надійшла до редакції 27.10.25