Single-Crystal Microwires Based on Doped Bi for Anisotropic Thermoelectric Devices

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Abstract **– We have investigated the possibility to use a microwire of BiSn to design an anisotropic thermoelectric generator. The glass-coated microwire of pure and Sn-doped bismuth was obtained by the Ulitovsky method; it was a cylindrical single-crystal with orientation** $(10\underline{1}1)$ **along the wire axis; the C3 axis was inclined at an angle of 70º to the microwire axis. It is found that doping of bismuth wires with tin increases the thermopower anisotropy in comparison with Bi by a factor of 2 – 3 in the temperature range of 200 – 300 K. For a Bi microwire with a core diameter of 10 µm with a glass coating with outer diameter of 35 µm, the transverse thermopower is ~ 150 µV/(K*cm); for BiSn, 300 µV/(K*cm). The design of an anisotropic thermogenerator based on BiSn microwire is proposed. The miniature thermogenerator will be efficient for power supply of devices with low useful current. In addition to the considerable thermopower anisotropy of BiSn wires in a glass coating, they exhibit stable thermoelectric properties, high mechanical strength and flexibility, which allows designing thermoelectric devices of various configurations on their basis.**

Index Terms **– anisotropy, bismuth, microwires, thermoelectricity, thermogenerator.**

I. INTRODUCTION

The search for new unconventional sources of electric power is now the research trend of particular concern and high priority.

As a source of heat for thermoelectric generators, the thermoelectric method of thermal energy conversion into electric energy involves unconventional renewable sources of thermal energy: from solar energy to the heat of human body. [1,2]

The appearance of new more efficient materials for anisotropic thermoelements (ATs) is reviving interest in the transverse thermoelectric effect. The efficiency of ATs is governed to a considerable extent by thermopower anisotropy value. The principle of operation and the features ATs were extensively studied both in scientific and applied aspects [3,4].

A transverse AT, as a voltage source in measuring systems, has some advantages:

(i) The thermopower, unlike a conventional thermocouple, is proportional to the temperature gradient (T1 - T2) / h instead of the temperature difference T1 - T2. Thus, decreasing the width h, it is possible to increase voltage at the same temperature difference.

(ii) Voltage V is proportional to length l; thus, it is possible to increase voltage by increasing the length of the plate.

(iii) To obtain voltage, we need no junctions that are required for increasing sensitivity. In the case of ATs, it is sufficient to increase the length of the crystal employed in order to enhance sensitivity.

In this regard, there are some problems in obtaining efficient ATs: the problem of material science, including obtaining of high-performance materials with high thermopower anisotropy and reproducible parameters, and the problem of the design, calculation, and preparation of devices based on ATs.

Bismuth single crystals exhibit a thermopower anisotropy of ≈ 50 µV/K in a temperature range of 100 – 400 K, which makes it possible to design ATs with a sensitivity of ≈ 10 – 15 mV/W and rapid response time τ = 10-2 s; they find practical application, in particular, as heat flow meters in microcalorimetry [5,6].

The value and temperature dependence behavior of the thermopower anisotropy of Bi can be rather easily controlled by doping and introduction of twin interlayers [7]. Bismuth turned out to be appropriate in various radiation sensors and microelements. The fundamental difference of ATs from traditional thermoelements is that the thermopower comprises the geometric factor l/h, where l is the sample length and h is its thickness. The thermopower of traditional thermoelement does not depend on the geometric sizes of these thermocouples, whereas the thermopower of ATs is proportional to the length and inversely proportional to the thickness; thus, we can increase the thermopower by increasing the AT length.

II. SAMPLES AND EXPERIMENT

We have studied the possibility of using a microwire of bismuth doped with Sn to design an anisotropic thermoelectric generator. Glass-insulated single-crystal wires of pure and Sn-doped bismuth were prepared by the Ulitovsky method; they were cylindrical single crystals with the $(10\underline{1}1)$ orientation along the wire axis; the C_3 axis was inclined at an angle of 70° to the wire axis. The technique described in [8,9] allows preparing single-crystal wires with diameters from 50 µm to nanometers. It is known that the size effect significantly changes the thermoelectric properties and leads to an increase in thermoelectric efficiency [10].

The developed technology allows obtaining a glass-insulated single-crystal microwire of Bi and its alloys with Sn with a length up to a few meters and with a given diameter from 100 nm to 50 µm. The specific resistivity was studied as a function of the doping impurity composition, wire diameter, and crystallographic orientation.

To study the thermopower anisotropy of the wires, we used samples with C_3 oriented along the wire axis, which were obtained by the methods of zone and laser recrystallization.

The transverse thermopower $\alpha_{trans} = U/\Delta T$, where U is the voltage across the sample, ΔT is the transverse temperature gradient. To measure the transverse thermopower α_{trans} in microwire segments with a length of 10 cm, we made a special device consisting of two copper plates with different temperatures. A glass-insulated microwire segment with a length of 10 cm was placed between these plates in such a way as to keep good thermal contact between the glass cover of the microwire and the surface of the plates throughout the length of the microwire (Fig. 1). To obtain a uniform temperature gradient, a resistive heater was placed on one of the plates; it occupied 80% of the entire surface of the plate. The temperature gradient was measured by a differential copper-constantan thermocouple, two junctions of which were situated in the middle of the plates near the surfaces being in contact with the microwire.

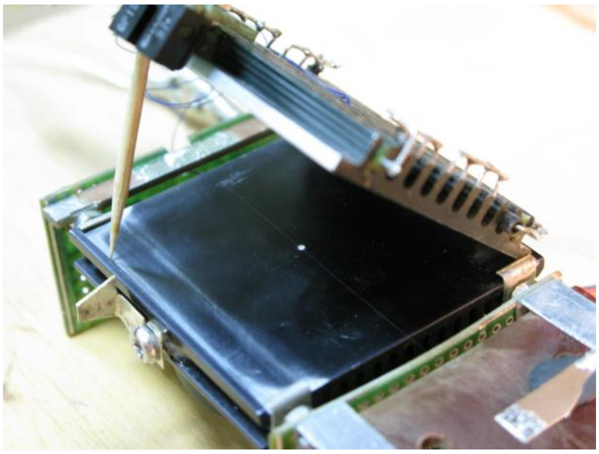

Fig. 1. Physical form of the device for measuring transverse thermopower in samples of a glass-insulated microwire.

The method of ShdH oscillations was used for estimating the Fermi level in doped Bi wires.

III. RESULTS AND DISCUSSION

Fig. 2 shows the diagram of rotation of the transverse magnetoresistance of the Bi- 0.05 at% Sn wires with (a) the (10$\underline{1}$1) standard orientation and (b) C_3 orientation along the wire axis. The angular dependence of the transverse magnetoresistance (TMR) R(Θ) in the Bi-0.05at%Sn wires with the (10$\underline{1}$1) orientation along the axis is similar to dependence for bulk samples: the dependences are symmetric about directions $\Theta = 0^o$ and $\Theta = 90°$. At $\Theta = 0$, $H \parallel C_3$; at $\Theta = 90°$, H is parallel to the binary axis C_2.

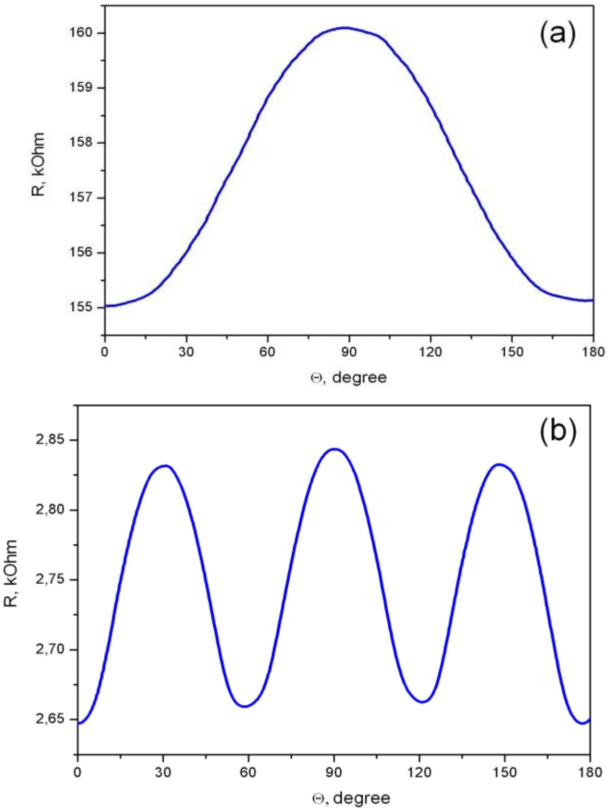

Fig. 2. Angle diagrams of TMR *R(Θ)* of Bi–0.05Sn (*d* =0.6 µm) with standard (*a*) and trigonal (*b*) orientations, *H* = 0.5 T, *T* =4.2 K.

In wires with C_3 oriented along the wire axis, the anisotropy of the transverse magnetoresistance is governed only by L-carriers, because, as the magnetic field rotates in the basal plane, the contribution of T-holes to the magnetoresistance does not depend on the direction. The rotation diagram structure corresponds to the sixfold rotation axis symmetry. The minima in the diagrams correspond to the sample orientation when one of the binary axes C_2 is parallel to *H*.

Fig. 3 depicts the dependences of the longitudinal magnetoresistance (LMR) R(H), $H \parallel I$ for the Bi-0.05 at% Sn wires with the (10$\underline{1}$1) and (111) orientation along the wire axis and ShdH oscillations at $H \perp I$ for wires with C_3 oriented along the wire axis.

Fig. 3 shows that ShdH oscillations of the magnetoresistance R(H) in Bi wires doped with an acceptor impurity of Sn can be seen in the longitudinal and transverse orientations both in wires with C_3 oriented along the wire axis and in wires with the (10$\underline{1}$1) orientation along the axis. Analysis of the SdH oscillations (Fig. 3) shows that the glass-insulated single-crystal Bi-0.05 at% Sn wires under study really had two orientations: C_3 along the axis and $C_{½}$ along the wire axis.

The Fermi energy of holes in T in the Bi-0.05 at% Sn wires was calculated in terms of the two-band Kane model using the expression 1.

$$\varepsilon_F^T = \varepsilon_{par} - \frac{1}{2}\varepsilon_g^T + \left[\varepsilon_{par}^2 + \left(\frac{1}{2}\varepsilon_g^T\right)^2\right]^{\frac{1}{2}} \qquad (1)$$

Where ε_{par} is the energy in the parabolic band approximation;

$$\varepsilon_{par} = \frac{eh \cdot \Delta_T^{-1}}{2\pi c \cdot m_c^T} \qquad (2)$$

is the Fermi energy of holes in T calculated downwards from the band top in T; m_c^T is the small cyclotron mass of T-holes; ε_g^T is the gap in the T-point of the Brillouin zone that amounts to 200 meV according to [11,12]; Δ_T^{-1} is the value of inverse period of the ShdH oscillations from the smallest section of the hole ellipsoid in the T-point of the Brillouin zone.

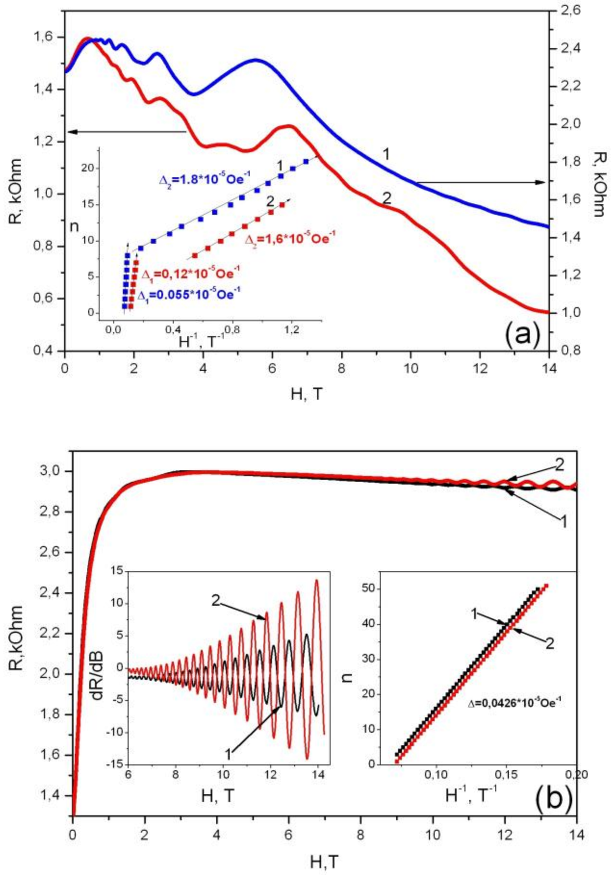

Fig. 3. *(a)* Field dependencies of LMR *R(H) (H||I)* of Bi-0,05 aт% Sn wire (*d* = 1 μm) with standard $(10\bar{1}1)$ (1) and trigonal (2) orientations at *T* = 2.1 K. Insert: dependences of the quantum number n of the ShdH oscillations on reverse field H^{-1}. *(b)* Field dependencies of TMR *R(H)* ($H \perp I$) of Bi-0,05 aт% Sn wire with trigonal orientation at $\theta = 0°$ (1) and $\theta = 67°$ (2) according to figure 2 (b), at *T* = 2.1 K. Inserts: left – field dependencies of derivative of TMR at $\theta = 0°$ (1) and $\theta = 67°$ (2) at *T* = 2.1 K; right - dependences of the quantum number n of the ShdH oscillations on reverse field H^{-1} at $\theta = 0°$ (1) and $\theta = 67°$ (2) at *T* = 2.1 K.

In addition, it was taken into account that at H || I, as in wires of pure Bi of the given crystallographic orientation [9], the ShdH oscillations are registered from the cross-section of the hole T-ellipsoid close to the maximum (the sample axis is tilted by an angle of 20° from the bisector axis). It was found that ε^T_F in Bi-0.05 at% Sn wires is located in the zone of L-holes.

To study the anisotropy of the thermopower and resistance, the temperature dependences *α(T)* and resistance R(T) of Bi–0.05 at% Sn wires with different orientations in a temperature range of 4.2 – 300 K were investigated (Fig. 4). Fig. 4 shows that the maximum thermopower anisotropy occurs at temperatures of 250-300 K; it is 100-120 μV/K, which is more than twice as high as the anisotropy α in pure Bi in the same temperature range.

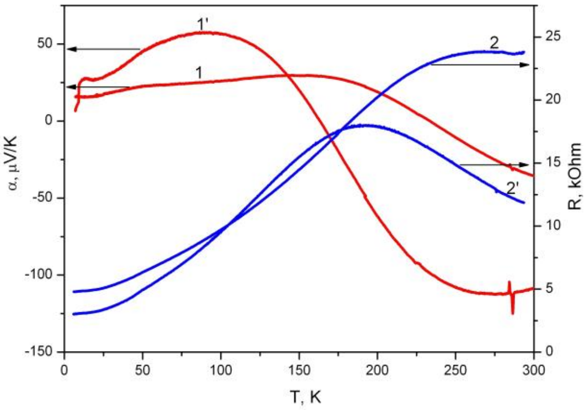

Fig. 4. Temperature dependences of thermopower *α(T)* (scale on the left) and resistance R(T) (scale on the right) of Bi–0.05 at% Sn wires (*d* =0.6 μm) with standard (1,2) and trigonal (1',2') orientations.

The transverse thermopower of glass-insulated microwire segments with a length of 10 cm of Bi and Bi-0.05 at% Sn in the diameter range d = 3 – 20 μm was measured at room temperature; the diameter D involving the glass insulation varied within 15 – 40 μm. The highest transverse thermopower per unit length of the microwire equal to 100 μV/(K*cm) was obtained for a bismuth microwire with d = 8 μm. For the Bi-0.05 at% Sn microwire, the maximum transverse thermopower per unit length of the microwire is significantly higher: it is 290 μV/(K*cm) in a microwire with d = 5.5 μm.

These results allow expecting that, after finding the optimum design solution of the place of a long microwire in the plate in the external temperature gradient, it will be possible to prepare an anisotropic thermoelectric generator for feeding devices with low useful current.

In addition to the considerable thermopower anisotropy, glass-insulated BiSn wires exhibit stable thermoelectric properties and high mechanical strength, which allows designing thermoelectric devices of various configurations on their basis. The fact that the efficiency of an anisotropic generator comprises the wire length and thickness yields broad possibilities of their optimization; the efficiency and the economic feasibility of the process of preparation of the wires will enable applying them as anisotropic generators on an industrial scale.

IV. CONCLUSION

It is found that doping of bismuth wires with tin increases the thermopower anisotropy in comparison with Bi by a factor of 2 – 3 in the temperature range of 200 – 300 K. According to the results, for a Bi microwire with a diameter of 10 μm with a glass coating of 35 μm, the transverse thermopower is ~ 150 μV/(K*cm); for BiSn, 300 μV/(K*cm), that can be used to create ATs for feeding devices with low current.

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