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Thermoelectric Properties of InSb Whiskers

A.A. Druzhinin, I.P. Ostrovskii, Yu.M. Khoverko, N.S. Liakh-Kaguy

Lviv Polytechnic National University, 12, S. Bandera St., 29013 Lviv, Ukraine

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The article deals with studies of thermoelectric parameters of InSb whiskers with tin concentration of about $4.4\cdot10^{18}$ cm^{-3} in the temperature range 4.2-300 K. The resistance and Seebeck coefficient were measured experimentally. The InSb whiskers have shown rather high values of Seebeck coefficient exceeding the values of bulk materials by 2-3 times. Using a special method of heat transfer in the whisker joints, the thermal conductivity of the whisker was simulated. The obtained threshold on the temperature dependence of thermal conductivity for InSb whiskers and nanowires in the range of about 100 K connecting with phonon capture of charge carriers indicates high reliability of the data obtained. As a result, ZT parameter of InSb whiskers versus temperature in the temperature range 4.2-300 K was calculated. The obtained value of ZT parameter 0.15 at room temperature indicates a possibility of the whisker use for thermal converters design.

Keywords: Whiskers, InSb, Thermo-emf, Thermal conductivity, Figure of merit.

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1. INTRODUCTION

InSb nanowires (NWs) doped with Sn impurities with diameters of about 10 nm are expected to have ZT ~ 3 at 300 K [1]. Large thermovoltage values exceeding 1 mV could be induced in thermoelectrical converter consisting of a single InSb NW that is promising for electronics [2]. The average value of the figure of merit in a temperature range 400-800 K for intrinsic bulk InSb material was found to be $0.42\cdot10^{-3}$ K^{-1} [3]. Besides, parameter ZT of Sn-doped InSb NWs is 0.002-0.006 at 300 K [4] which is lower than that for bulk material [3] with three times lower thermal conductivity as well as a substantially smaller Seebeck coefficient. The results of [5] indicate a decrease of thermoelectric power in NWs (to ~ 62 % of the bulk value) as the wire radius is initially reduced. Besides, high values of the parameter ZT are hard to achieve in InSb material due to its high thermal conductivity of ~ 17 Wm^{-1}K^{-1} [6]. Thus, most research on InSb material has focused on reducing its large thermal conductivity [7]. Nevertheless, high values of the parameter ZT of ~ 0.6 (at 637 K) for Te-doped InSb single crystals [8] report on the prospect studies of their thermoelectrical properties of such micro- and nanomaterials.

The aim of this work is to study the temperature dependence of the kinetic coefficients of the conductivity σ, the Seebeck coefficient S and the thermal conductivity χ in the temperature range 4.2 to 300 K, and the estimation of the parameter ZT of InSb whiskers with a tin concentration of about $4.4\cdot10^{18}$ cm^{-3} and their comparison with the thermoelectric parameters of massive samples.

2. EXPERIMENTAL METHOD

In order to measure the temperature dependences of the electrical conductivity of InSb whiskers in a wide temperature range, the equipment of the International Laboratory of High Magnetic Fields and Low Temperatures was used. The electrical resistance was measured with a voltmeter B7-21 accurate to ± 0.1 % Ohm. The signals of two thermocouples placed at the ends of the sample that measured the ambient temperature were averaged.

Investigation of the behavior of electrical and thermal conductivity of InSb whiskers at temperatures 4.2-300 K was carried out in this way. The specimens under study were placed on a special insert in a helium cryostat, where they were cooled to a temperature of 4.2 K. The samples were heated to room temperature with a special insert with a heater made of bituminous wire wound on the body of the insert.

The stabilized electric current of 1-100 μA in the measuring circuit was given by the current source Keithley-224. The electrical voltage at the samples contacts as well as the output signal of the thermocouple were measured by Keithley-2000 digital voltmeter with an accuracy of 1 μV, with simultaneous automatic registration of displays through a parallel port of the personal computer and their visualization on the monitor screen.

In order to study the thermoelectric thermal conductivity of InSb whiskers in the temperature range 4.2-300 K, a four-contact method for the manufacture of contacts was used. This technique was as follows: two contacts were placed in the middle part of the crystal, and two others – in the same plane, but at the ends of the whisker. Contacts at one end of the crystal were used as a heating element, in which the stabilized current was passed. With the help of the heating element, a temperature gradient along the axis <111> between the next two crystal contacts (thermoelectric branch) was created, on which the thermoelectric cell was measured. The distance between the contacts on which the temperature gradient was measured is an order of magnitude larger than the distances between the other contacts and is approximately 10 mm. This allowed to avoid the influence of contacts on the value of the measured thermoelectric power.

Since the length of the thermoelectric branch is large enough, it is easy to create a temperature gradient during heating of the hot end only a few degrees. In addition, due to the large length of the thermoelectric branch (approximately 10 mm), even with a significant increase in the temperature of the hot end, the temperature of the cold end remains unchanged. The temperature of the hot end was determined by measuring the resistance of the sample and taking into account its temperature dependence of the resistance in the temperature range 4.2-300 K. The cold end temperature was controlled using a Cu-Cu <Fe> thermocouple with an accuracy of 0.1 K.

To determine the coefficient of thermo-emf the following procedure was used. At first, measurements of the resistance of the resistive branch at a temperature $R(T)$ in the range of 4.2 to 300 K were carried out. Next, this dependence can be used to determine the temperature of the hot end of the sample. Then measurement of the Seebeck coefficient takes place.

The proposed method for determining the thermoelectric coefficient allowed to measure the temperature, as well as the temperature gradient along the whisker's axis with high accuracy (about $3 \cdot 10^{-2}$ mV/K for 4.2 K).

2.1 Method of Determination of Thermoelectric Parameters of Whiskers

Fig. 1 illustrates a schematic diagram of a method where 2-whisker joints are depicted: 1-4 and 2-3.

The method is carried out in the following manner. At the ends of the whisker in the form of a joint, the point contacts 1, 2, 3, 4 are created. They are connected to the ends of the joints 3-4 (warming up the branch), and 1-2 (measuring branch). The contact is also created in the middle of the joint 0.

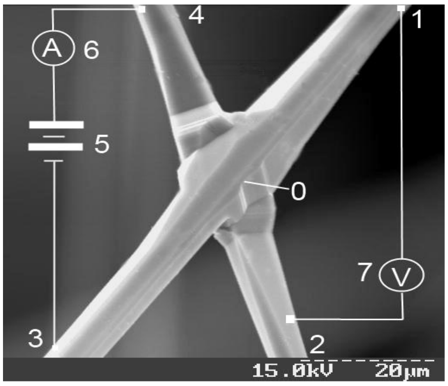

Fig. 1 – Scheme of implementation of the method for determining thermoelectric parameters of the whisker

The heating current I from the source of the stabilized current 5 is passed through a heating medium, namely, through two adjacent contacts, through the section 3-0-4, its value is controlled by milliampermeter 6. Two other contacts 1-0-2, which simultaneously form a measuring branch, are alternately connected to the middle of the pinch 0. The universal digital device 7 measures the potential difference between the contacts 0-1 (U_1), between the contacts 0-2 (U_2), and then measures the resistance between the points 1-2 of the measuring field R_3 and the current through it I_3. Using a microscope, the length of the longest part and shorter measuring branches are measured and the cross-sectional area of the crystal S is determined.

The heating of the medium by current I of the heating unit creates two heat fluxes to the points of the 1 and 2 measuring line, which are written as $W_1 = \chi S/l_1 \Delta T_1$ and $W_2 = \chi S/l_2 \Delta T_2$ (χ is the thermal conductivity coefficient). And taking into account that the temperature gradients ΔT_1 and ΔT_2 can be expressed in terms of thermocouple magnitudes $U_1 = \alpha\Delta T_1$ and $U_2 = \alpha\Delta T_2$, and that the difference in heat flux creates electric power between points 1 and 2, we obtain the formula

$$I_3^2 R_3 = \frac{\chi S}{\alpha l_1}\left(nU_2 - U_1\right),, \quad (1)$$

where $n = l_1/l_2$. Formula (1) is used to determine the ratio of the coefficients of thermo-emf and thermal conductivity χ/α.

3. AN ANALYSIS OF THE THERMOELECTRIC PARAMETERS OF THE InSb WHISKERS

The kinetic properties of n-InSb whiskers doped with tin admixture were studied in the temperature range from 4.2 K to room temperature (~ 300 K). As a result of the studies, the dependences of the kinetic coefficients $\sigma(R)$, S and χ on the temperature T (see Fig. 2, Fig. 3 and Fig. 4, respectively) were obtained. This allowed to find thermoelectric quality factor $ZT = \sigma s^2 T/\chi$ [9]. The corresponding temperature dependence of the thermoelectric characteristics of InSb whiskers is presented in Fig. 5.

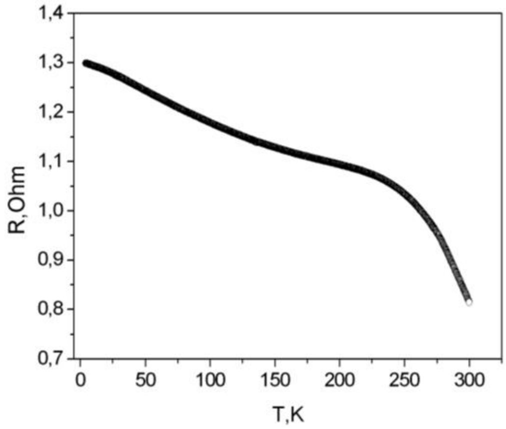

Fig. 2 – Temperature dependence of the resistance of InSb whiskers with an impurity concentration of $4.4 \cdot 10^{18}$ cm^{-3}

Investigation of the temperature dependence of the resistance of InSb whiskers with an impurity concentration of $4.4 \cdot 10^{18}$ cm^{-3} (Fig. 2) was carried out in the temperature range of 4.2 to 300 K. The following features of the whiskers as a sharp drop of resistance in the range 225-300 K were observed. At low temperatures, the resistance of InSb whiskers increases.

The temperature dependence of the whisker resistance R is opposite to its conductivity σ. Thus, we can consider the temperature behavior of the whisker conductivity in comparison with that for bulk material. On the temperature dependence of the conductivity σ of massive samples of n-InSb with different concentrations of dopants, a minimum at 250 K was experimentally found [10]. With an increase in the concentration of impurities, the position of the minimum conductivity shifted towards higher temperatures while its absolute magnitude decreased [10]. The presence of a minimum in σ was due to an increase in the contribution to the conductivity of the electron-phonon scattering in the temperature range of the Debye temperature. For large concentrations of the impurity at these temperatures, conductivity is due to the scattering of charge carriers by the ionized atoms of impurities, therefore, there is no minimum in the temperature dependence of σ, and only the threshold is observed, which is fixed in Fig. 2. At temperatures $T > 300$ K, a transition to zone conductivity was detected.

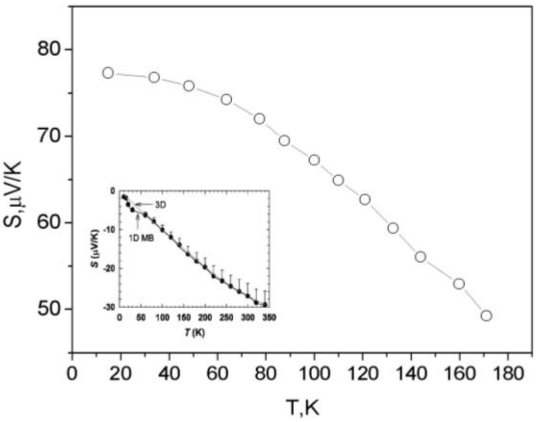

Fig. 3 – Dependence of the Seebeck coefficient on temperature for InSb whiskers. Insert: dependence of the Seebeck coefficient on temperature for *p*-type InSb NWs with a concentration of impurities of $7 \cdot 10^{15}$ cm^{-3} [11]

An analysis of the results of the investigation of InSb whiskers has shown that the Seebeck coefficient (Fig. 3) smoothly increases to 70 μV/K at a temperature of about 100 K, where there is a threshold, and with an increase in temperature above 100 K, a gradual increase in the Seebeck coefficient occurs. For comparison, in the insert in Fig. 3 the dependence of the Seebeck coefficient on temperature is shown for the InSb NWs of the *p*-type conductivity with the concentration of impurities of $7 \cdot 10^{15}$ cm^{-3}. The insert in Fig. 3 shows a shoulder on the dependence of S on T corresponding to the temperature of 50 K. In the experimental dependences of the Seebeck coefficient of the whiskers, a shoulder was detected at a temperature of 100 K. The probable cause of the appearance of this shoulder on the temperature dependences of the Seebeck coefficient is the phonon capture of the carriers, which takes place in both *n*-type and *p*-type semiconductors [12]. We know [13] that the phonon capture of charge carriers increases with a decrease in the concentration of doping impurities and shifts towards lower temperatures, which is observed in the experimental dependences (Fig. 3).

With regard to the absolute value of the Seebeck coefficient, there are considerably higher values of the Seebeck coefficient for whiskers than for NWs. The high values of the Seebeck coefficient for investigated whiskers indicate their promise for the use in sensors of thermal quantities.

On the basis of the study of the nature of heat dissipation in InSb whisker joint, according to formula (1), the ratio of thermal conductivity to Seebeck coefficient χ/α was determined in the temperature range 4.2-300 K. The obtained ratio χ/α allowed to simulate the temperature dependence of the thermal conductivity in the temperature interval 5-300 K. The results of the simulation are shown in Fig. 4. The results obtained to raise their reliability should be checked using 3ω method [14]. Nevertheless, the obtained values of the whisker thermal conductivity are in good accordance with literature data [15].

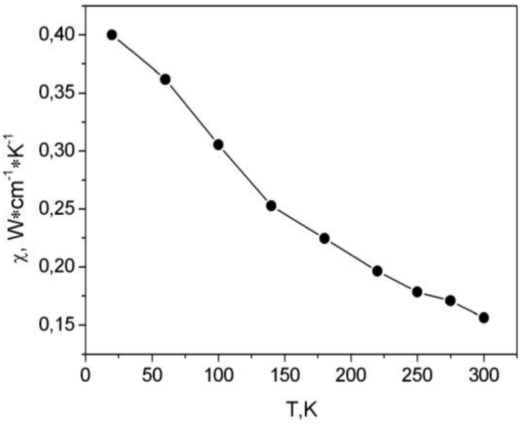

Fig. 4 – Thermal conductivity versus temperature for InSb whiskers with an impurity concentration of $4.4 \cdot 10^{18}$ cm^{-3}

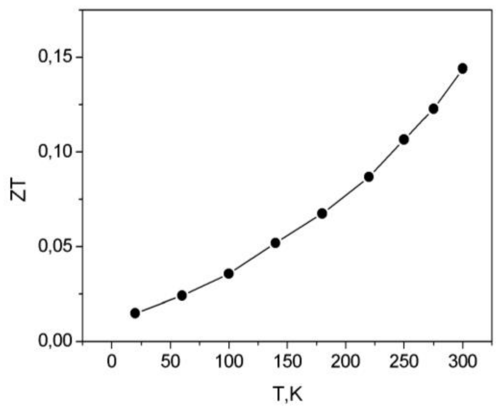

Fig. 5 – ZT parameter versus temperature for InSb whiskers with an impurity concentration of $4.4 \cdot 10^{18}$ cm^{-3}

Taking into account the results obtained for kinetic coefficients of InSb whiskers (Fig.2, Fig.3 and Fig.4), one can calculate the temperature dependence of parameter ZT. The results of such simulation according to Eq. (1) are presented in Fig. 5. It is obvious from Fig. 5 that the value of parameter ZT for room temperature 0.15 is rather high in comparison with literature data [16]. The authors of [1] have shown the maximum value of thermopower σs^2 for $T = 300$ K in InSb crystals, which was connected with carrier scattering by polar optical phonons. However, the value is strongly dependent on the crystal concentration and could vary in the temperature range. Thus, we have not observed the above non-monotonic dependence of the whisker thermopower in the range of room temperatures.

Let us discuss the next phenomenon observed in InSb whiskers at low temperatures. The whisker magnetoresistance was shown to oscillate according to arising Shubnikov-de-Haase oscillations in magnetic fields

[17-19]. One can suppose that thermo-emf oscillations could arise when the whiskers were loaded in magnetic field. This fact needs to be checked because possible oscillations restricted substantially the use of InSb whiskers as thermoelectric materials at low temperatures. On the other hand, InSb is a middle-temperature thermoelectric material. Thus, its application is promising for temperatures more than 300 K, where all oscillations disappear.

4. CONCLUSIONS

The dependences of resistance and Seebeck coefficient on temperature for InSb whiskers with a tin concentration of about $4.4 \cdot 10^{18}$ cm^{-3} in a temperature range 4.2-300 K were studied. The whiskers were shown to have rather high values of the Seebeck coefficient as compared with bulk material and InSb NWs. The use of the whisker joints allows us to simulate the temperature dependence of the whisker thermal conductivity due to the analysis of heat fluxes. The obtained value of the whisker thermal conductivity is in good accordance with literature data. Taking into account the temperature dependences of the whisker conductivity, Seebeck coefficient and thermal conductivity, parameter ZT has been calculated in a temperature range 4.2-300 K. The obtained value of the parameter ZT in whiskers at room temperature exceeds the value of bulk material by a factor of 3 that is promising for design of thermal converters with thermoelectric principle of action on their base. The high values of the Seebeck coefficient for investigated InSb whiskers indicate their promise for the use of thermal quantities in sensors.

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Термоелектричні властивості ниткоподібних кристалів InSb

А.О. Дружинін, І.П. Островський, Ю.М. Ховерко, Н.С. Лях-Кагуй

Національний університет «Львівська політехніка», вул. С. Бандери, 12, 29013 Львів, Україна

У статті розглядаються термоелектричні параметри ниткоподібних кристалів InSb з концентрацією олова близько $4{,}4 \cdot 10^{18}$ см$^{-3}$ в інтервалі температур 4,2-300 K. Температурні залежності опору кристалів та коефіцієнта Зеебека вимірювали експериментально. Встановлено, що ниткоподібні кристали InSb мають досить високі значення коефіцієнта Зеебека, що перевищують значення масивних зразків у 2-3 рази. При використанні спеціально розробленого методу передачі тепла у зростках ниткоподібних кристалів проведено моделювання їх теплопровідності. Отримане плече на температурній залежності теплопровідності ниткоподібних кристалів та нанодротів InSb в області близько 100 K, що пов'язане з явищем фононного захоплення носіїв заряду, свідчить про надійність отриманих даних. У результаті була розрахована температурна залежність параметра ZT ниткоподібних кристалів InSb в інтервалі температур 4,2-300 K. Отримане значення параметра ZT 0,15 при кімнатній температурі вказує на можливість використання ниткоподібних кристалів для створення термоперетворювачів.

Ключові слова: Ниткоподібні кристали, InSb, Термо-ерс, Теплопровідність, Термоелектрична добротність.