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# Glass-encapsulated Single-crystal Nanowires and Filiform Nanostructures Fabrication

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## ABSTRACT

This paper reports on the production technology, features and practical application of capabilities of glass-coated micro- and nanowires fabricated by casting from the liquid phase. Micro- and nanowires with diameters from 80 nanometers to 1 micron have been received using improved technology of microwire casting by Ulitovsky method. The authors offer a technology of thinning such wires, as well as new manufacturing techniques of the filiform composite nanostructures on their basis. Some physical properties of the received micro- and nanowires have been investigated.

**Key words:** nanowire, nanostructure, microwire, cast, semimetal, semiconductor, thermoelectric.

## 1. INTRODUCTION

This line of investigation applies glass-coated cast microwires fabrication technique. As it is known, this technology has been invented in former Soviet Union by prof. A.V.Ulitovsky and it was successfully applied and developed in many respects due to design at the "ELIRI" Research Institute in Chisinau (Republic of Moldova) [1] The named institute has also accumulated wide experience on the practical use of such microwires [2-4].

Growing interest in nanowires has been inspired by extension of the range of materials, such as semiconductors, semimetals, magnetic and superconducting ones, used for nanowires fabrication. Some of them have been previously applied to fabricate cast microwires (with diameter more 1 microns) both for research purposes and development of sensing devices [4-7]. Upon transition to nanometer dimensions, special properties of practically one-dimensional structures offer the challenges for their new applications. First of all, it is the question of quantum size effects to be observed in one-dimensional semiconductor filaments widely investigated in the semiconductor physics right along [8, 9]. "Magnetic flux quantization effect in the normal, non-superconducting state" has been first discovered in the submicron monocrystal bismuth filaments obtained by liquid phase casting [9].

The single-crystal structure of nanofilaments and their high degree of perfection proved to be an important feature of quantum size effect phenomenon. It has been described in the papers [9, 10] that ***Bi*** filaments obtained through liquid phase casting are monocrystal ones. Clear pattern of Shubnikov – de Haas oscillations made it possible to determine that Dingle temperature in ***Bi*** filaments lies within the range of 0.4 -1 K.

For almost 10 years by now many research groups have been studying Bi-based nanowires fabricated by using various techniques: electrodepositions, etching of constrictions, the method of melted material injecting into pores of various dielectric matrices ($Al_2O_3$ , $B_2O_3$ etc.) by applying of hydrostatic pressures [11-19]. Today the range of materials used for making nanowires is rather broad, including those with semiconducting, semimetallic, magnetic and superconducting properties.

Extensive research materials have been gathered and new physical effects discovered and predicted in such filaments being of interest in the first place from the scientific standpoint. It should be noted that Huber [11, 12] was the first to obtain ***Bi*** nanowires with $\mathbf{C_3}$ longitudinal orientation lengthwise the wire. Maximum value of thermoelectric figure of merit **Z** has been predicted for filaments of this crystallographic orientation.

L.D. Hicks and M.S. Dresselhaus have predicted appearance of semimetal-semiconductor transition in bismuth nanofilaments with $d < 30$ nm, owing to quantum size effect, which will result in sharp (almost by the order of magnitude)

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increase in thermoelectric power and, accordingly, figure of merit at 300 K already [13]. This problem is actual especially in view of the possibility to create most effective thermoelectric microcoolers applied in microelectronics on the basis of high-temperature superconductors.

In the paper presented by Hereman the above-described theoretical predictions received proof on experimental grounds [14]. Exceptional result has been obtained – thermoelectric power value in nanowire arrays with $d$<10nm has come to thousands of μV/K, though filaments resistance makes only several GOhm. Unfortunately, the authors were not in a position to assess the thermoelectric figure of merit $Z$ and even the power factor $|\alpha|^2\sigma$, as the number of filaments in the dielectric array composite had not been determined.

In this context the study of single filaments or FCNS based on nanowires with their known number is exceptionally important both as a research matter and for the future practical applications [20-22].

## 2. TECHNOLOGICAL ASPECTS OF FABRICATION CAST NANOWIRES

It appears from the described above that transition to wires with a thread diameter less than 0,2 microns ( that is 200 nanometers), promises new interesting applications. But manufacturing of such cast nanowires in glass insulation with a diameter of thread less than 500 nanometers has become possible only due to series of developments of a usual process of cast microwires.

The process of cast micro- and nanowires fabrication consists of the following steps:

- Levitation melting of a certain amount of conducting material (metal, semimetal, semiconductor) placed in a glass tube within the high-frequency electromagnetic induction field;
- Heating-up to soften the end of such tube holding a drop-shaped conducting material and formation of micro-bath as a glass coating flowing around the suspended drop;
- Capillary drawing from the lower end of this glass tube (e.g. by way of coiling on a rotating spool), the capillary to be filled with molten thread-forming material from the drop of metal, semimetal or semiconductor;
- Cooling of the drawn filament to form the mentioned cast microwire in glass coating for crystallization of the thread and solidification of the glass insulation.

There are two classic variants of obtaining cast microwire in glass insulation by A.V.Ulitovsky's method: drop process briefly described above, and uninterrupted process. In the second method an iron core (allocated inside a glass tube) is fed from above at the zone of inductor, and by gradually melting on the end, the metal core fills up the metal which moved from a micro-bath to the inside of a capillary to form a microwire thread (fig. 1) [1].

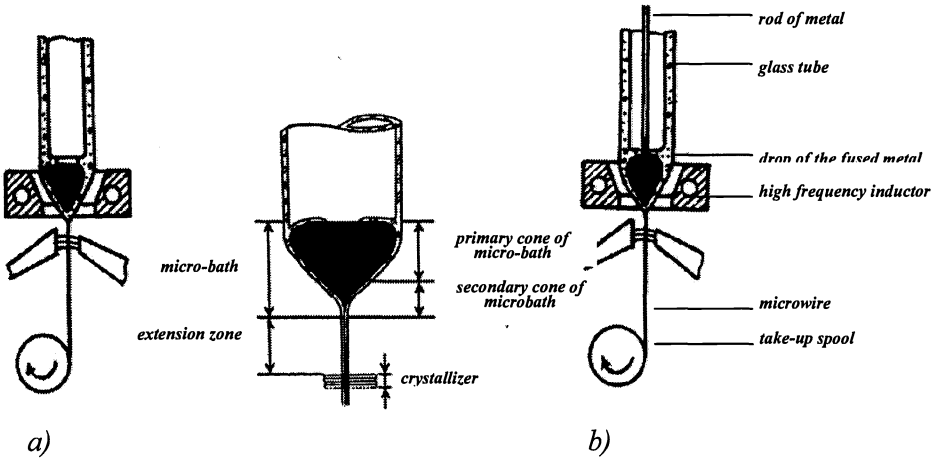


Fig. 1. Obtaining of micro- and nanowires in glass insulation from the liquid phase of the metals, semimetals and semiconductors by method of A.Ulitovsky
a) drop method; b) continuous method

Typical Ulitovsky's technology allows to continuously obtain microwires from various metals and metal alloys, with thread diameter from 2 up to 50 microns using drop process method with thread diameter from 5 up to 100 microns using continuous process method. By using additional techniques for the drop process technology in Eliri Institute some thinner microwires with thread diameter 0,08-0,8 microns from a number of metal alloys and semimetalls (***Bi, Sb, Bi-Sb***) (i.e. nanowires) have been received.

Obtained single nanowires from ***Bi*** and $Bi_{0,88}$-$Sb_{0,12}$ alloys with thread diameter 200 - 800 nanometers have strictly single-crystal structure (as well as semiconducting and semimetal microwires with thread diameter > 1 microns). The density of dislocations, determined on microwire samples from Bi with the diameter decreasing down to 5 μm, does not exceed $10^3 \div 10^4 cm^{-2}$. We assume that conditions of crystallization of the nanowires promote the quality of filiform crystal of the thread and even smaller number of dislocations.

It is necessary to note, that modification of the drop version of the Ulitovsky's method is most suitable for obtaining micro- and nanowires from semiconductors and semimetals. In this case it is possible to provide reliable protection for the micro-bath outside and inside the glass tube through inert gas, and to control with more flexibility input parameters of the casting process, as well as the thread composition of the obtained nanowires.

Therefore, the present work studies the opportunities of obtaining nanowires based on the drop process. First we want to note, that during formation of micro- and nanowires there is a physical restriction on the minimal radius of a capillary, which the molten metal can enter. As is well known, when temperature is higher than melting temperatures of metal alloys, semiconductors and semimetals behave - from the point of view of hydro-dynamical properties, which is the most important for the technology of casting - as pure metals melts, differing mostly in capillary constant $\kappa = \sigma/\gamma_g$ , where $\sigma$ - surface-tension of a melt, and $\gamma_g$ - its density.

When a layer of oxide on the boundary line between a melt and glass is absent, the minimal radius of a capillary, which a liquid melt of the forming thread can initially enter, can be estimated in a first approximation by expression:

$$r = \sigma_{mw} / (p_0 - v\gamma w / \eta) \qquad (1)$$

where $\sigma_{mw}$ - interfacial tension on boundary line a metal melt – glass,

$p_0$ - absolute pressure in a tube above a micro-bath,

$v$ - velocity of crystallization,

$\gamma$ - density of melting,

$\eta$ - viscosity,

$w$ – work of the adhesion forces, per unit of surface area.

Here it is assumed, that after formation of an empty glass capillary the pressure in it is hundreds times less than atmospheric pressure. It follows form here, that for reducing the initial diameter of a microwire it is necessary to select a glass, which provides the minimal value of the interfacial tension between the glass and the melt in the micro-bath. Usually such selection allows to reach an interfacial tension (at casting temperatures) of about half of the value of the surface tension $\sigma_v$ of such melt in vacuum. The quantitative estimation gives value of $r$ equal about several microns for many materials. For example, for ***Bi*** the estimated value of the initial minimal diameter of a microwire thread $d_i = 2r = 3{,}5$ microns.

However, after the melt enters the capillary and during the continuation of the process of nanowire drawing, the condition of the further joint flow of the glass capillary with the melt inside changes, and the reduction of the thread diameter becomes possible. If the melt mass in the microbath does not exceed the so-called critical mass, (which is supported in the suspended condition completely at the expense of ponderomotive forces of an electromagnetic field of the high-frequency inductor), the geometric parameters of the drawn micro- and nanowires depend mainly on properties of the glass tube (its geometry, viscosity, and surface tension) and main parameters of the technological process (speed of capillary drawing, strength of an electromagnetic field of the inductor, micro-bath temperature, and speed of the tube feeding).

A set of parameters stands out of this combination, since they affect directly the geometry of the forming ninowire, and they can be considered as the defining parameters of the casting process. Experimental and theoretical research has shown, that the dependence of the thread diameter of micro and nanowires on these parameters is described by the formula:

$$d = k_T \eta_c^{4/3} / (\gamma_g \sigma_g^{1/3} v_{dr}^{2/3}) , \qquad (2)$$

where $\eta_c$, $\gamma_g$ and $\sigma_g$ - viscosity, density and surface tension of glass, correspondingly; $v_{dr}$ - speed of a capillary drawing; $k_T$ - dimensionless empirical coefficient dependent on a number of additional technological parameters (in our experiments $k_T \sim 1 \cdot 10^{-6}$).

As it is seen from expression (2), theoretically there are no obstacles for reduction of the diameter of nanowire threads, which requires increase of the speed of capillary drawing and decrease of glass viscosity. The latter requires an increase of microbath temperature, as glass viscosity decreases with the rise in temperature under the exponential law. However, in practice slightest non-uniformity of glass, microvibration of winding or feeding device, extraction of gas dissolved in melt or glass, oscillation of a current in the high-frequency inductor and other destructive factors, result in a breakdown of the thread inside a capillary tube or to a full breakaway of the latter, especially when the general diameter of the glass capillary is small ($D < 3\mu m$).

Therefore, for obtaining nanowires with thread diameter less than 500 nanometers it is necessary, apart from of increase of temperature of the microbath and capillary drawing speed, to increase essentially thickness of glass isolation, to achieve special stability in activity of mechanical and electrical units of the installation, to use glass tubes of a particular purity, and also to use special additional technological methods in order to maintain stability of temperature and geometric dimensions of the micro-bath stretching cone. By this method we received ***Bi*** nanowires in glass insulation with minimal thread diameters of the order of 0,1 microns.

As our experiments and N.Berman's theoretical calculations show (Berman was the first to solve Stefan's problem for conditions of crystallization of cast microwire), super-cooling is a necessary condition for crystallization of the abovementioned wires. The expression he received for the temperature field along the drawn out filament has a minimum (temperature "hole") in the liquid phase before the crystallization front. Without it, in conditions of the rapid relocating of a drawn filament and presence of the heat-insulating glass layer, the heat, liberated under crystallization, would not have an opportunity for a sufficient outflow to the liquid phase [1]. Although super-cooling, especially the concentration one, usually promotes formation of many crystallization centers, in our case when it is caused by the kinetic factors, emersion of the additional crystallization centers and development of dislocations is blocked by high moving speed of the inter-phase boundary at the formation of micro- and nanowire thread.

Another important aspect of obtaining cast nanowire, which considerably influences its electrophysical properties, is the condition of nanowire crystallization. As it is known, crystallization of micro- and nanowires in glass insulation has some peculiarities in comparison with the growth of typical crystals. Because of the high drawing speed, solidification of the thread depending on its composition can take place both with crystallization, and without it (when formation of amorphous structure occurs). In each case solidification occurs in conditions of deep super-cooling which takes place even for one-component materials. Super-cooling for casting of micro- and nanowires has kinetic character unlike the concentration super-cooling, which is possible at low crystallization speed of non-casting nanowires from two-component alloys, and depends on constitution diagrams of these alloys [23]. The super-cooling effect is easily observed during the procedure of micro- and nanowire casting.

However, Berman's kinetic model does not provide adequate quantitative description of the phenomenon of the melt super-cooling before the crystallization front. Therefore, it appears impossible to directly use the results of his thermalphysic calculations in order to optimize the modes of ninowire casting. In particular, his formulas for determination of coordinate of the crystallization point of the ninowire thread $x_{cr}$ and the depth of the melt super-cooling $\Delta T_{sc}$, give negative values under the logarithm sign when using reference values for thermalphysic parameters for many semiconducting and semimetallic materials, and therefore these formulas lose their physical sense.

It happens because the given model assumes a priori the equality of specific heats of melting $L_m$ and crystallization $L_{cr}$. This is fair only for equilibrium crystallization at the melting temperature $T_m$. However, in conditions of a deep supercooling $\Delta T_{sc}$ it is necessary to take into account the dependence of $L_{cr}$ on the minimum temperature $T_{min}$ in some zone before the crystallizatin front. The experimental data about such dependence in the literature is insufficient. Therefore we will use the theoretical dependence implied from the thermodynamic definition of the crystallizatin heat with allowance for the temperature dependence of Gibbs energy. According to [24] it looks like:

$$L_{cr} = L_m (1 - \Delta T_{sc} / T_m) = L_m (1 - T_{min} / T_m). \quad (3)$$

By analogy to Berman's model, but taking into account for above-stated regarding $L_{cr}$ we can record a one-dimensional problem of quasistationary crystallization of ninowires as follows:

$$d^2\theta_i/dX^2 - \mathrm{Pe}\, d\theta_i/dX - \mathrm{Bi}\,\theta_i = 0, \quad (i = 1, 2) \tag{4}$$

$$\theta_1(X)\,|_{X=0} = \theta_{mb}, \tag{5}$$

$$\theta_1(X)\,|_{X=X_0} = \theta_2(X)\,|_{X=X_0} = \theta_m, \tag{6}$$

$$d\theta_1(X)/dX|_{X=X_0} - d\theta_2(X)/dX|_{X=X_0} = \chi_0 \mathrm{Pe}\,[\theta_1(X_{min}) + T_a], \tag{7}$$

$$\theta_2(X)\,|_{X\to\infty} = 0, \tag{8}$$

where $\theta(X) = T_i(X) - T_a$, ($i = 1, 2$) - excess temperature; $T_a$ - absolute environmental temperature; $X = x / r_0$ - dimensionless coordinate; $x$ - current coordinate; $r_0$ – ninowire thread radius; $X_0 = x_{cr} / r_0$ - dimensionless coordinate of the crystallization point; $\mathbf{Bi} = 2\alpha_{th} r_0 / \lambda$ - Bio criterion; $\mathbf{Pe} = c\,\gamma\,v\,r_0 / \lambda$ - Peclet criterion; $\chi_0 = L_m / cT_m$ - dimensionless parameter, which determines conditions of the melt supercooling above the crystallization front; $\alpha_{th}$ - effective coefficient of the thread heat emission; $c$, $\gamma$, $\lambda$ - specific heat, density and heat conduction of the thread, correspondingly; $v$ – nanowire drawing speed. Conditional point of the beginning of the capillary tube formation (that is the bottom drop surface) is accepted as the coordinates origin ($x = 0$). The axis of coordinates is directed vertically downwards. The radius $r_0$ of a drawn out thread is assumed to be constants.

For convenience of calculations all parameters and variables except of temperature are shown in a dimensionless form. In the given statement we have neglected the distinction between thermalphysical parameters in liquid ($i = 1$) and solid ($i = 2$) phases, as well as the availability of a glass shell. Taking these factors into account would not increase essentially the accuracy of calculations[1]. Therefore at a first approximation we can use this simpler model. (4) - (8). The boundary conditions here are obvious. Temperature of a thread at initial point $X = 0$ is equal to the micro-bath temperature: $\theta(0) = \theta_{mb} = T_{mb} - T_a$. In the point of phase transition $\mathbf{X_0}$ temperatures of liquid and solid phases are identical and equal $\theta_m = T_m - T_a$. The boundary condition (7) describes temperature gradient in the crystallization point with allowance for the ratio (3). On infinity, thread temperature becomes equal to the enviromental temperature.

Our model differs from the Berman's only by its dimensionless form and constant coefficients, which take into account, however, temperature dependence on a specific heat of melting. The solution of the circumscribed problem is the following:

$$\theta_1(X) = \theta_k \cdot e^{\varepsilon_2 \cdot X} + \frac{\chi_0 \cdot Pe(\theta_m + T_c)}{2\beta} \cdot e^{-\varepsilon_1 \cdot X_0} \cdot \left(e^{\varepsilon_1 \cdot X} - e^{\varepsilon_2 \cdot X}\right) \tag{9}$$

$$\theta_2(X) = \theta_k \cdot e^{\varepsilon_2 \cdot X} + \frac{\chi_0 Pe \cdot (\theta_m + T_c)}{2\beta} \cdot \left(e^{-\varepsilon_2 \cdot X_0} - e^{-\varepsilon_1 \cdot X_0}\right) \cdot e^{\varepsilon_2 \cdot X} \tag{10}$$

where $\beta = \frac{1}{2}\sqrt{Pe^2 + 4Bi}$; $\varepsilon_1 = \frac{Pe}{2} + \beta$; $\varepsilon_2 = \frac{Pe}{2} - \beta$. (11)

Position $X_0$ of the crystallization front is determined from (10) or (11) when $\theta_1(X) = \theta_m$ by analogy with [1]:

$$X_0 = \frac{1}{-\varepsilon_2} \cdot \ln \frac{\theta_{mb}}{\theta_m - (\theta_{\min} + T_a) \cdot \chi_0 \cdot Pe/2\beta}. \tag{12}$$

Determining an extremum of the function $d\theta_1(X)$ and taking into account, that $\varepsilon_2/2\beta \approx$ **-Bi/Pe**, $\varepsilon_1/2\beta \approx$ **1 - Bi / Pe$^2$** and **Bi / Pe <<1** , we receive obvious expression for the temperature minimum in liquid phase:

$$\theta_{min} = \frac{2\cdot\beta\cdot\theta_m}{\varepsilon_1}\cdot\left(-\frac{\varepsilon_2}{\varepsilon_1}\right)^{\frac{\varepsilon_2}{2\cdot\beta}}\cdot\frac{1-\frac{\chi_0\cdot Pe\cdot T_a}{2\beta\cdot\theta_m}}{1+\frac{\chi_0\cdot Pe}{\varepsilon_1}\cdot\left(-\frac{\varepsilon_2}{\varepsilon_1}\right)^{\frac{\varepsilon_2}{2\cdot\beta}}} \quad . \tag{13}$$

As in [1] $\theta_{min}$ does not depend on temperature of the micro-bath, and is mainly determined by the mode of cooling of the received nanowire. The increase of the Bio criterion, for example, when intensity of the cooling rises, raises $\theta_{min}$, that is reduces the depth of super-cooling. With increase of the casting speed, the depth of super-cooling increases.

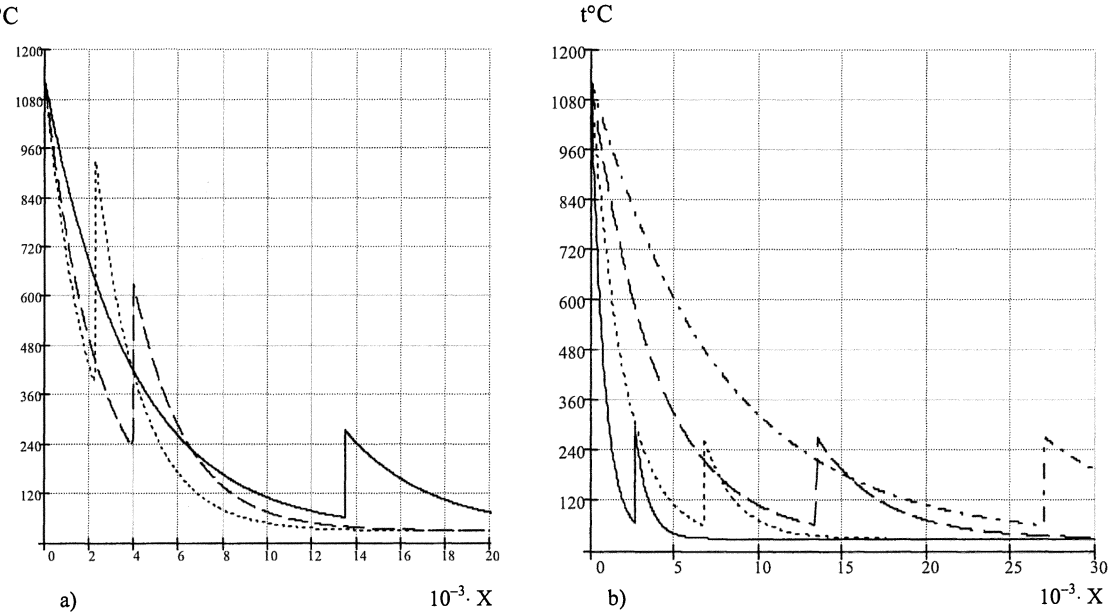


Fig.2 Distribution of temperature along the nanowire

a) Different materials:
***Bi*** ( ····· ) Pe = 0.271; Bi = $7.08\cdot10^{-5}$
***Sb*** ( – – – – – ) Pe = 0.085; Bi = $3.67\cdot10^{-5}$
***Ge*** ( ——— ) Pe = 0.118; Bi = $5.97\cdot10^{-5}$

b) Material - ***Bi*** . Criterion Bi = $3.54\cdot10^{4}$
Criterion Pe :
0.271 ( ——— ) 1.354 ( – – – – – )
0.677 ( - - - - - - - - ) 2.708 ( ·-·-·-·-· )

The extreme attainable temperature of cooling of the liquid phase is from (13) at **Pe** $\rightarrow \infty$ by the rule of the Lopitale. As distinct from Berman's model, we have:

$$\theta_{min\,abs} = [\lim \theta_{min}]_{Pe\to\infty} = (\theta_m - \chi_0 T_a) / (1 + \chi_0) = T_m / (1+\chi_0) - T_a \,. \tag{14}$$

It follows from here, that the extreme attainable minimum of temperatures in liquid phase before the crystallization front $T_{min\,abs} = T_m / (1+\chi_0)$, and the limiting depth of supercooling is determined by the formula:

$$\Delta T_{sc\,max} = T_m - T_{min\,abs} = \chi_0 / (1+\chi_0) = L_m T_m / (c T_m + L_m) \quad (15)$$

Thus, the account of dependence of the crystallization heat from the temperature results in dependence of limiting depth of super-cooling on temperature of melting: when $T_m$ increases the depth of extreme possible super-cooling $\Delta T_{sc\,max}$ also increases, having, however, a physical limitation equal $L_m / c$. The calculation gives values of the limiting super-cooling for nanowires from ***Ge*** about 590 K, from ***Sb*** - 410 K, from ***Bi*** - 209 K.

Typical distribution of temperature along the drawned out nanowire, calculated according to the formulas (9) and (10) for different thermophysical parameters, is shown on fig. 2. Obtained curves demonstrate visually the kinetic character of super-cooling of the liquid phase: with increase of Bio criterion, that is with increase in nanowire drawing speed, the depth of supercooling will increase.

According to the conventional view, for doped materials at high speeds of cooling crystallization without diffusion occurs. In case of casting semiconducting and semimetalic nanowires, it requires, in our opinion, a more detailed study, since there is experimental data referring to the growing of arborescent straps from ***Ge***, which put these assertions under doubt [25]. In particular, a phenomenon of inversion of segregation coefficient at the crystallization front, and periodic character of distribution of impurity in such objects, were discovered. We have all the reasons to assume, that analogous processes can occur at casting nanowires, since crystallization speeds here are even higher. The theoretical substantiation of such distribution can be received if we take into account finiteness of the diffusion rate of impurities in a melt in comparison with the speed of shifting of crystallization front.

Although, as it is mentioned above, through raising melting speed and temperature of the micro-bath, it was possible to receive nanowires with thread diameters of about 80 - 100 nanometers, its further reduction meets seriouschnological difficulties, if it remains within the framework of the classical technology by Ulitovsky. In this regards, we have proposed and developed a new technology of local nanowire thinning by a short-term laser heating of cast nanowires with diameter from 100 up to 1000 nanometers with its simultaneous stretching. Thus, we have obtained the so-called "bridges" with diameter below 20 nanometes, and length up to 0.5 mm, which served for the research of their properties [5, 20].

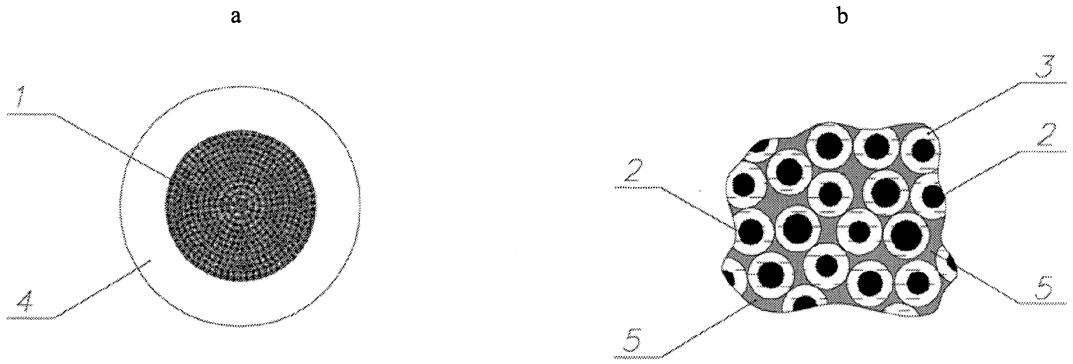


Fig.3. Cross-section of filiform composite nanostructure: a – ful wiew; b – megascopic wiew.
1 – bundle of nanowires; 2 – thread of nanowire; 3 – glass insulation of nanowire;
4 – glass covering of FCNS; 5 – material for filling space between nanowires

However, for further practical application of nanowires, increase of their length and assembly them in composite nanostructures is desirable. The direct way to receive such nanostructures is to assemble single nanowires in a bunch with length up to 200 mm and to subsequently sinter them with each other with softening of glass isolation. The drawback of this technology is that the structure of nanowire threads (from Bi and its alloys) is broken due to the low melting temperature of these materials. Besides, the distance between conducting nanofilaments in a matrix appears to be too big because of the thick isolation of single nanowires.

Therefore, one of the authors of this article has proposed a design and technology of obtaining filiform composite nanostructures (FCNS) through high-speed stretching of the microwire bunch with melting and repeated crystallization of threads and their simultaneous thinning to the diameter of 8-50 nanometers. Proposed design of FCNS, consists of many thousands nanowires with length of more than 50 mm, closed in a shared glass envelope with overall diameter 40-80 microns (fig.3). For some materials the length of nanowires reaches 700 mm which is important for implementation of medical microthermocouples.

## 3. RESEARCH OF SOME PHYSICAL PROPERTIES OF CAST NANOWIRES

We should note that the nanowires obtained in the pores of thin films and plates are only 50-150 microns in length. This restrains many applications of such structures, in particular creation of highly sensitive microthermocouples to be used for biomedical investigations and diagnostic bolometers, development of probe microcoolers for deep cooling of local zones and points inside the human organism (e.g. in case of treating the oncological diseases), high-frequency current thermal converters, miniature moisture sensors, microcoolers for power-consuming microcircuits, processing units in computers, etc.

Though the research of FCNS properties has not been done yet, there are all grounds to assume that their application for the mentioned items will be no less perspective, because of expected increase in it the thermoelectromotive and thermo-electro Z-factor. The inclusion opportunity in such structure of nanowires from various materials will allow expanding of their effective range of temperatures owing to averaging properties of separate materials. At this stage, mainly properties of single micro- and nanowires were investigated.

While studying mechanical properties of filamentary crystals based on Bi and its alloys by breakdown test and by the microindentation method there was found a scale effect - the decrease of microhardness $\sigma_p$ with the wire diameter decreasing [26]. An important peculiarity of wires of semimetals based on ***Bi*** and alloys $Bi_{1-x}Sb_x$ is that they are single crystals and possess high structural perfection. It was found that in wires ($d > 20$ μm) $Bi_{1-x}Sb_x$ the density of dislocations approaches or is equal to the density in bulk crystals ($N_D=10^6 \div 10^7$ cm$^{-2}$), and with the diameter decreasing down to 5 μm the density of dislocations becomes equal to $N_D=10^3 \div 10^4$ cm$^{-2}$ [27]. Perfection of the crystal structure of filamentary crystals of ***Bi*** and its alloys increases with their diameter decreasing.

Besides, it was found that the limit of elastic deformation of thin wires of semimetals is an order larger than the analogous value for bulk samples and at low temperatures (4.2-77 K) it achieves the values of 2.5-3% relative elongation, this being close to the theoretical value. This will allow in principle to use thin wires based on ***Bi*** and its alloys in tensometry [28].

Availability of distinct diagrams of rotation of the transverse magnetoresistance and the **ShdH** oscillations allow to conclude that the wires are single crystals and have a strict orientation along the wire axis for all the diameters and compounds of ***Bi*** and ***Bi-Sb***, and the Dingle temperature for Bi wires was 1 K.

The resistance, magnetoresistance and thermopower of wires ***Bi***-12at%***Sb*** and ***Bi***-12at%***Sb*** doped with ***Sn*** up to 0,01at% in the temperature range 4.2-300 K in the magnetic fields up to 14 T were investigated. The elastic stretch of the wires was used as an instrument for changing the gap and changing $\varepsilon_{FG}$ in alloys $Bi_{1-x}Sb_x$.

Fig. 4 shows the temperature dependences of the resistivity $\rho(T)$ for wires ***Bi***-12at%***Sb*** of different diameters. For the samples with $d>18$ μ the ratio of the resistivity $\rho_{4.2}/\rho_{300}$ is 530. A significant growth of the resistance at $T<10$ K indicates good structural quality of the samples ***Bi***-12at%***Sb*** and small degree of compensation by uncontrolled acceptor and donor impurities.

At room temperature the resistivity of the wires $0,3\ \mu<d<60\ \mu$ does not practically depend on diameter. At 4.2 K decrease of the resistivity with the diameter decreasing is observed. It is known that in wires of pure ***Bi*** an inverse effect is observed - increase of the resistivity with $d$ decreasing connected with the classical size effect (CSE) and caused by an additional scattering of the carriers by surface [29].

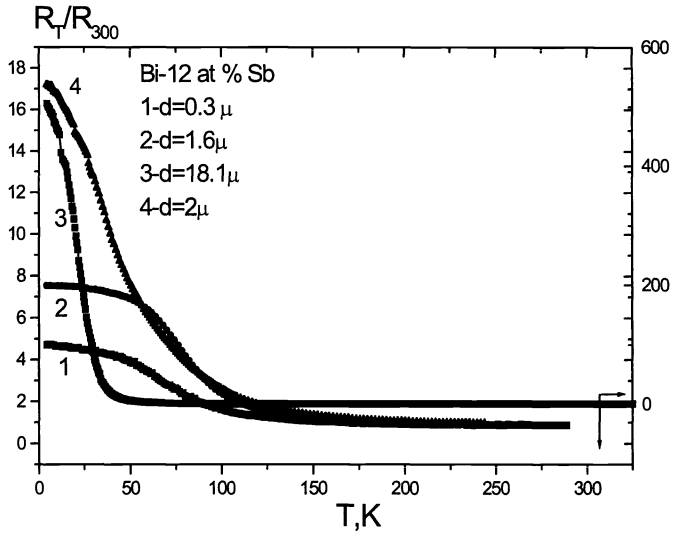


Fig. 4 Experimental temperature dependence of the resistance of ***Bi***-12at%***Sb*** nanowires of various diameters normalized to the resistance at 300K.

In the case of wires $Bi_{1-x}Sb_x$ the resistivity decrease may be due to the increase of the charge carrier concentration caused by the bending of the surface potential, its influence increasing with the wire diameter d decreasing. An analogous effect is observed in films [4]. In this case a decrease of the band gap $\Delta E_g$ must be observed. Hence, it is necessary to calculate the band gap width in alloys $Bi_{1-x}Sb_x$. Availability of distinct exponential sectors on the dependences ln $\rho(1/T)$ in the temperature range 40-140 K allowed to estimate $\Delta E$ for wires of all diameters.

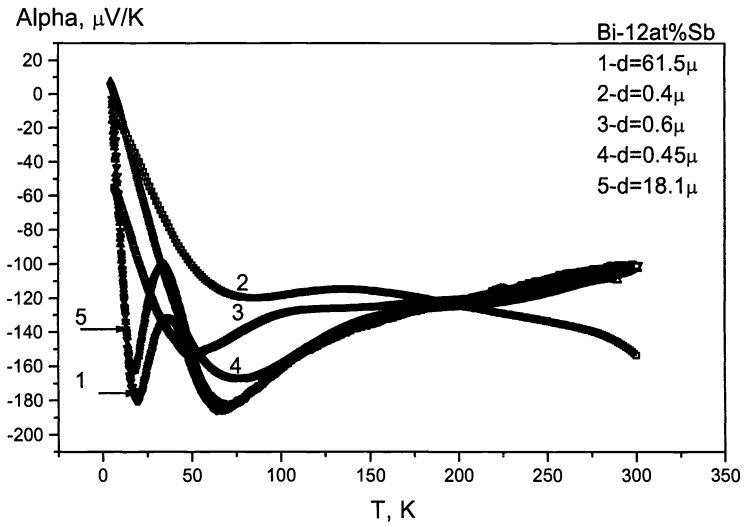


Fig. 5. The temperature dependences of the thermopower $\alpha(T)$ for ***Bi***-12at%***Sb*** with different diameters.

It is known that bulk ***Bi***-12at%***Sb*** crystals are the best thermoelectric materials for n- branch at 80K. However, bulk crystals are very fragile. The advantage of thin wires in a glass cover is their higher mechanical strength and possibility for creation of elastic anisotropic deformations up to 1.5-2% relative elongation. On fig. 5, 6 show the thermopower and P.f. of ***Bi***-12at%***Sb*** wires different diameters.

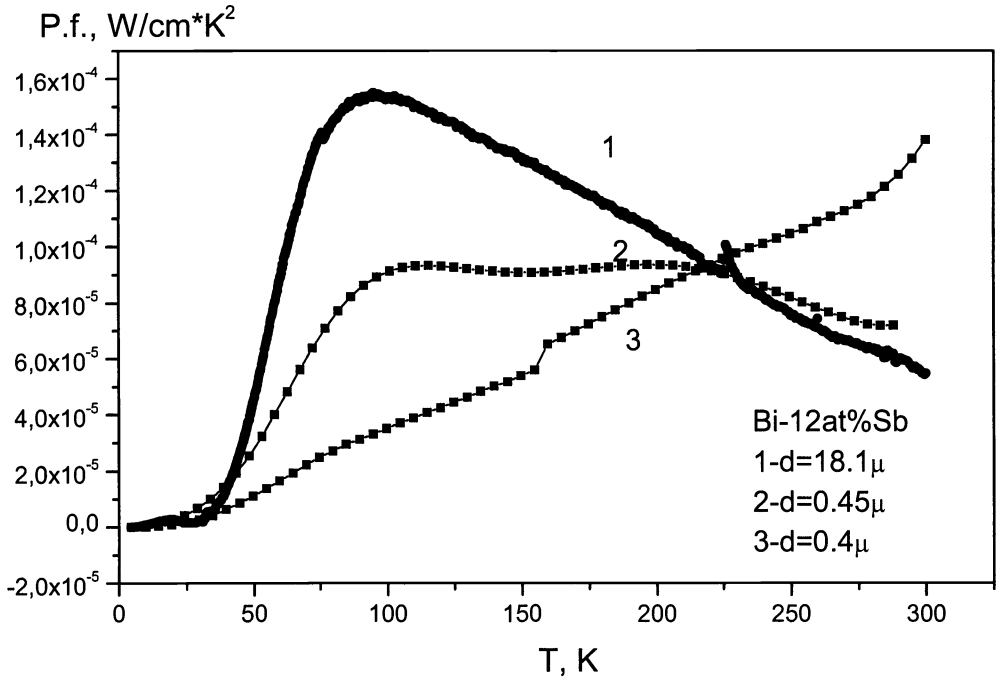


Fig. 6 Temperature dependence of the Powder factor of ***Bi***-12at%***Sb*** nanowire of various diameters.

It was found that the maximal power factor in ***Bi***-12%***Sb*** wires is $(1\ldots2)\cdot10^{-4}$ W/cm*K$^2$ in the temperature interval of 100-150 K.

As stated above, one of the most important characteristics of nanowire casting technology is superhigh speed of thread crystallization that may come up to 10 million and even more degrees per second. At that the limits of mutual solubility in semiconductor materials' solid solution components sharply extend, which generates formation of compound semiconductor solid solutions possessing some new properties still awaiting in-depth studies and major applications. Forced entrainment into the capillary as well as quick "congelation" of even mutually insoluble components allows obtaining metastable homogeneous (almost atomic-level) mixtures, which seems to be promising too.

Thus, in nanowires with abnormal composition ($x$>10%) metastable solid $InSb_{1-x}$–$InBi_x$ solution thread, realizable only on following the given technology, the linear dependence of magnetoresistance on the magnetic field has been observed starting from zero induction. On their basis one can design weak and medium magnetic fields linear transducers, cheaper and more sensitive than Hall-effect devices. Picture 7 shows the dependence of magnetoresistance on the magnetic field induction for nanowires with thread diameters of 340 nm (upper curve) and 850 nm (lower curve) representing the fact that the given characteristics happen to be linear up to 0.7 T induction.

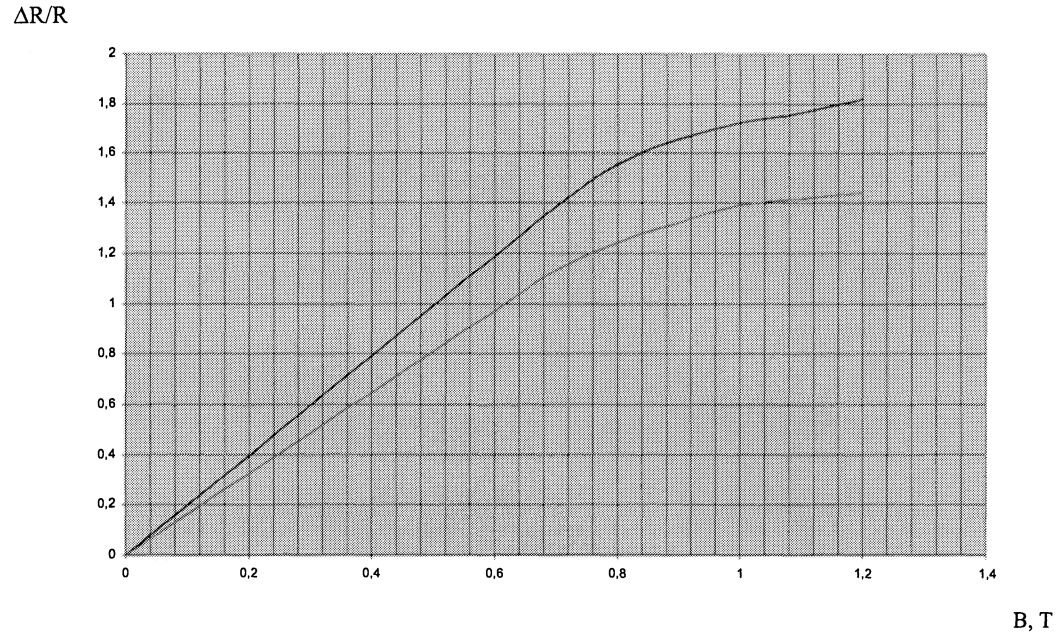


Fig. 7. Magnetoresistance of $InSb_{0.9}$-$InBi_{0.1}$ nanowires.
1 - 340 nm (———); 2 - 850 nm (– – – –)

High speed of cooling in nanowires promotes development of amorphous thread structure for many complex alloys, similarly to that previously obtained on cast microwires for metallic magnetic substances. They can found application in threshold devices, like Vigand elements, in paper documents encoding and protection systems, microwave radiation protection systems and anti-radar coatings. Previous experiments have shown that some semiconductor peritectic alloys ($In_3SbTe_2$ and $In_4SbTe_2$), possessing in addition the superconducting properties, also get amorphous or nanocrystall structure at such conditions of nanowire crystallization. These compounds are supposed to improve superconductivity parameters when in amorphous state.

## CONCLUSION

The carried out analysis has shown that use of single nanowires is perspective for investigation of electrophysical properties of quasi-one-dimensional structures. For their realization it is offered to use the technology of obtaining of cast microwire by the method of Taylor-Ulitovsky. The calculations give restriction to the minimal diameter of the capillary wherein the melt of a metal or a semiconductor from the microbath can penetrate in the initial moment of the nanowire formation. However, this does not prevent the nanowire core diameter from further decreasing in the process of stretching due to the growth of the velocity and decrease of glass viscosity. Theoretically there is no restriction to the core diameter decrease in the considered model. We have received cast nanowires in glass isolation from Bi with the thread diameter less than 100 nm by experiment

A specified analytical expression for the temperature field of stretched nanowire in the one-dimensional case with account of the crystallization heat dependence on the depth of overcooling is obtained. There were found values of kinetic overcooling of the core before the crystallization front achieving hundreds of degrees, this corresponding to the experimental data.

A technology for obtaining of composite nanostructures on the basis of cast nanowires of semiconductors and semimetals being perspective for practical use is offered. In contrast to known structures, one composite nanostructures can

contain glassed nanowires of various materials. This enlarges the working diapason of temperatures of thermoelectric devices on their basis.

The studied thermoelectric and galvanomagnetic properties of obtained nanowires of semiconductors and semimetals have confirmed single crystal structure of the core and have shown peculiarities of manifestation of size effects in semimetal and semiconductor wires based on ***Bi***. There were found the sign inversion and maximum formation of the thermopower in the positive region, its value and position depending on the wire diameter ***d***, significant linear magnetoresistance in weak magnetic fields, in wires $InSb_{0,9}$-$InBi_{0,1}$ , considerable increase of the wire strength, this being interesting from both scientific and practical viewpoints and opening wide perspectives for development of this direction.

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