LONG GLASS-COATED SEMIMETALLIC AND SEMICONDUCTING WIRES PREPARED BY TWO DIFFERENT LIQUID PHASE METHODS

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Cylindrical semimetallic and semiconducting wires have been fabricated by the glass-coated melt spinning (GCMS) and high-pressure injection and directional crystallization (HPIDC) methods. In the GCMS method, a certain quantity of desired conducting material is placed inside a glass tube and melted by induction heating in an inert atmosphere. When a capillary is drawing from the softened end of the glass tube containing the molten material, the latter is entrained inward the capillary to form a glass-coated wire, which is coiled on a winding drum. Under optimized fabrication conditions, this method enables to produce the flexible Pyrex-coated Bi wires with diameters from 100 nm to 10 \( \mu \)m and lengths up to several hundred meters. However, this method is inapplicable for fabrication of long wires from many semiconducting materials that greatly change their volume upon crystallization. For producing long lengths of high-quality wires, we used a new approach, which is based on pressure injection of molten material into the pre-evacuated quartz or Pyrex microcapillarities and unidirectional equilibrium crystallization along the wire axis direction. Features of the HPIDC fabrication steps are described. Using the novel HPIDC approach, we were able to grow InSb, PbTe, Ge, Bi, Sb, and Bi\(_{1-x}\)Sb\(_x\) wires with diameters ranging from \(~3\) to \(~1000\ \mu\)m and up to 20 cm in length.

1. INTRODUCTION

Thin semimetallic and semiconducting micro- and nanowires and their composites are now attracting growing interest due to their promising technological applications as magnetoresistance elements in wide-range magnetic-field sensing devices [1-3] and as thermoelectric elements with a high figure-of-merit in solid-state cooling devices [4]. These wires may have a combination of electronic, optical and mechanical properties that make them attractive for a large number of other engineering applications, including sensors to quantitatively measure heat and stress with very high sensitivity (see, e.g., Ref. 5), laser microdevices, and so on. Thicker bismuth and bismuth-bearing alloy wires (about 1 mm in diameter) are required for other applications such as thermal fuses and solders [6].

Previously, several methods of wire fabrication have been reported, including the Taylor method [7], high-pressure injection (HPI) of the liquid material [8-10], electrodeposition [1,11] and vapor-phase [12] methods. These methods have been applied to fabricate a variety of metal, semimetal and semiconductor wires embedded in a dielectric shell or matrix. For example, the Taylor technique, which consists of melting the starting material in glass tubes and drawing a fiber from the softened glass, has been used to making glass-coated Bi wires with diameters from 2.6 to 29 \( \mu \)m [7]. The HPI method was applied by Gurvitch [8] to the filling with Bi of thick-walled Pyrex pipes from 0.2 to 150 \( \mu \)m in inside diameter. It is clear that a similar HPI technique can be used to produce an array or network of micro- and nanowires embedded in a porous dielectric template. Recently, the HPI technique has been employed to fabricate the short Bi nanowire arrays with single-crystalline structure for thermoelectric applications [9,10]. Polycrystalline Bi [1] and Bi\(_2\)Te\(_3\) [11] wire arrays have been also fabricated by electrodeposition. The structure and physical properties of these wire arrays are directly related to the origin and properties of the porous templates, such as pore size distribution, pore orientation, and surface roughness of pores.

The fabrication of continuous metallic wires by the glass-coated melt spinning (GCMS) method has been known for many years and is well described in the literature [13]. Initially this method, also called the modified Taylor technique, was developed and used by a Moldovan manufacturer “Mikroprovod” to produce on industrial scale the microwire coils from various metals and metallic alloys. This method combines melting, composite (glass-coated wire) forming and cooling into a single continuous process, unlike conventional multi-stage techniques. At present, the GCMS method
is used in our laboratory to produce flexible composite Bi wires with length up to several 100 m and ranging in diameter from about 100 nm to several micrometers. However, the GCMS method has several drawbacks (see below), which make it impractical for fabrication of continuous glass-coated wires of semiconducting compounds. To produce long lengths of semiconducting wires, we have proposed a HPI-based technique with several essential modifications of the conventional procedures. The purpose of this article is to describe the main features of the glass-coated melt spinning and high-pressure injection and directional crystallization (HPIDC) techniques, which are used in our laboratory for fabrication of the long composite semimetallic and semiconducting wires. In contrast to ordinary wire arrays [1,9-12], our wires can be explored individually and facilitate the study of the role and magnitude of anisotropy of many physical properties. Moreover, these single-core wires can be arranged together along their length to obtain an ordered array or bundle of any shape and size, as required by thermoelectric and other applications.

2. FABRICATION OF CONTINUOUS WIRES BY THE GLASS-COATED MELT SPINNING METHOD

The GCMS method has been used for more than 40 years to produce the glass-coated metallic wires with diameters from \( d < 1 \) \( \mu \)m up to 200 \( \mu \)m (see, for example, [13], p. 198). This method involves three material phases, namely the crystal, the melt and the glass tube or capillary, and may be regarded as a derivative form of the Taylor method [14].

The method of GCMS wire fabrication is distinct from the Taylor method in that it is based on using of a high-frequency electromagnetic field, which is capable to heat the conducting materials above their melting points and to sustain them in a suspension state. For many metals, semimetals and low-resistivity semiconductors with melting points below or close to 1000°C, the melt spinning can be carried out using the standard GCMS apparatus and conventional procedures, which are well described in the Russian literature [13,15]. One striking aspect of the GCMS method is the disparity in both quality and sizes between the easily cast metals and semimetals such as Cu, Ag, In, Bi, etc., and the hard-to-cast materials such as InSb, PbTe, Bi\(_2\)Te\(_3\), etc. The easily cast materials readily produce fine wires longer than 100 m, while the others produce only thick wires and those rarely exceed 1 m. As a rule, materials that do not interact chemically with the silica glasses at high temperatures and at the same time have low melting points and relatively poor mechanical properties belong to the easily cast type.

![Fig. 1. Schematic illustration of the glass-coated melt spinning process.](image-url)
The GCMS fabrication apparatus that is used in our laboratory was designed and produced at the Research Institute ‘ELIRI’ (Chișinău). Fig. 1 shows the simplified method of operation of the system. A small amount of the desired material is placed in a closed-end glass tube. This tube is fixed vertically after that a r.f. induction heater is used to increase the temperature of the conducting material above the softening point of the glass ($T_s \approx 700^\circ$C for Pyrex) as well as to hold up the drop-shaped molten bath formed at the bottom tube part in a semi-suspension state. Due to induction stirring, all the oxides rise to the melt surface blanketing the liquid metal. When the heated end of the glass tube containing the molten drop is drawn, the resultant capillary entraps the melt from the drop and forms a flexible composite fibre with metallic core, which is coiled on a winding drum. The tube movement downward makes good the shortfall of glass. The basic requirements for the successful preparation of continuous glass-coated wires by the GCMS method are the correct choice of the drop temperature and winding speed. Usually, the optimal operating temperature is chosen as a compromise between wetting activity of the melt and glass viscosity. The diameter and morphology of the core and the thickness of the envelope depend in a complicated manner on the parameters of the preparation process (molten drop temperature, winding speed) and high-temperature physical and chemical properties of metal and glass used.

Using the GCMS method, we were able to produce flexible Pyrex-coated bismuth wires with diameters from 100 nm to 10 $\mu$m. The melting was made in an argon atmosphere. Although the real drop temperature was very difficult to determine, it is estimated that in the case of wires with submicron diameters the superheat temperature is close to 800$^\circ$C relative to the melting temperature of Bi. The obtained composite wire with liquid core was air-cooled to room temperature. In our check experiments, during cooling the external glass surface was blown with an argon stream in order to change the cooling rate. However, as we concluded later, such blowing has no detectable influence on the transport properties of the as-drawn Bi wires.

Since drawing of the capillary filled with liquid material is carried out at very high winding speeds (1 - 30 m/s), the crystallization process takes place under strong non-equilibrium conditions. Also, a strong supercooling upon solidification of Bi is expected, which can lead to spontaneous crystallization of glass-coated wires. For Bi, there are numerous experimental data [16,17] on the crystallization of supercooled microdrops and particles of different diameters. An analysis of these data does not indicate the existence of some correlation between the volume of the molten Bi and the value of the supercooling temperature [17]. For Bi islands with diameters from 100 mm to 30 nm, the relative supercooling is almost the same and equal to (0.3-0.4)$T_m$, where $T_m = 271^\circ$C is the melting temperature of bulk bismuth.

Due to the high anisotropy of the surface energy, crystalline Bi tends to form planar growth features even upon rapid solidification on amorphous substrates. Presumably for this reason, the Bi core of the as-drawn composite wires is composed of highly-oriented monocristalline blocks, but the region between these blocks and the glass shell is highly disordered. This conclusion is, in particular, confirmed by our observations of the Shubnikov-de Haas effect and superconducting inclusions with $T_c \approx 6$ K and $\approx 4$ K on the same submicron wire sample [18]. The superconducting phases of Bi were not found in the as-drawn wires with $d \geq 1 \mu$m.

The great majority of Bi wires grow in two distinct crystalline directions. For wires with $d \geq 1 \mu$m and 4 $\mu$m $\leq d \leq 10$ $\mu$m, the long axis made an angle of about 19$^\circ$ with the $C_1$ axis in the bisector-trigonal plane $C_1C_2$; this wire orientation is the same as that observed previously in the submicron Bi wires by Brandt et al. [19] and in Bi nanowires by Zhang et al. [9]. For wires with 1 $\mu$m $\leq d \leq 4$ $\mu$m, the wire axis made an angle of $\sim 12$$^\circ$ with the $C_1$ axis in the $C_1C_2$ plane and the trigonal axis is at right angle to the wire axis. The origin of the observed dependence of the crystalline orientation on the wire diameter remains unknown. Unfortunately, the GCMS process does not permit to provide control of the axial thermal gradient during the wire growth.

For several composite wires with core diameters from 3 to 10 $\mu$m, the glass envelope was removed by chemical etching in a solution of hydrofluoric acid. It was observed that the obtained free-standing Bi wires are very soft and have an extraordinary tensile ductility. These wires could be easily elongated up to 200% or bent in a $\vartheta$ - shape.
The main disadvantages of the GCMS method and the Taylor method (see, e.g., Ref. 8) are similar: (a) a strong superheating of the material relative to its melting temperature in order to soften the closed end of the glass tube, which may give rise to formation of undesirable oxides and silicates or to wire contamination with impurities from the glass; (b) a confined solidification, which leads to the appearance of mechanical stresses, cracks and/or pinholes due to the jumpwise volume change upon the liquid-crystal phase transition; (c) a rapid cooling below the crystallization temperature, which generates a large number of structural defects that affect the reproducibility of the wire properties; (d) wires with different diameters are obtained under different preparation conditions and, especially for this reason, have appreciably different structural quality and even diverse crystallographic orientations. Therefore, using the GCMS method, it is difficult to make really high-quality and extremely pure wires of identical bulk and surface properties with the same crystallographic orientation, which are needed to obtain useful size effect results [20,21]. Also, great care must be taken with processing of the experimental data to obtain significant information from measurements of the wire transport properties. To improve the structural quality of the as-drawn wires, they have to be subjected to additional post-preparation procedures, such as recrystallization or an optimized heat-treatment. As was shown in Refs. 7 and 22, the directionally crystallized wires differ from the as-drawn Taylor- and GCMS-wires in the sense that they have less structural defects, such as grain boundaries, twin interfaces, dislocations, etc. However, during recrystallization, the wire crystallographic orientation changes in an unpredictable way and a profound understanding of the recrystallization mechanism of wire-shaped Bi is yet to be achieved.

The melt spinning of Bi-Sb alloys was carried out using the same preparation parameters as those for pure Bi. As the Bi-Sb alloys have a pronounced tendency to segregate during solidification, the good-quality semiconducting Bi$_{88}$Sb$_{12}$ wires could be obtained only after the floating-zone procedure [22].

Enormous effort has been applied to the preparation of other semiconducting wires by the GCMS method since 1975. However, as our experience shows, the Taylor method and its GCMS version are practically inapplicable for preparation of long wires from many semiconducting materials of industrial importance, especially from those that greatly change their volume upon solidification such as InSb, PbTe, etc. For example, InSb expands by about 13% in volume upon crystallization. Therefore, it is no wonder that a good deal of strains is produced in the InSb core during its solidification in an enclosed space. We observed experimentally that the magnitude of these strains is so large that the they easily initiate cracks in the capillary walls and result in a cessation of the GCMS preparation process.

It is known that the HPI technique makes unnecessary the utilization of superheating conditions [8]. For fabrication of high-quality semiconducting wires, we have developed a new approach, which is a combination of the HPI and directional crystallization techniques, whereby long lengths of glass-coated wires can be grown from the molten state in one technological process without utilization of additional post-preparation procedures.

3. PREPARATION OF MONOCORE SEMICONDUCTING WIRES BY THE HIGH-PRESSURE INJECTION AND DIRECTIONAL CRYSTALLIZATION METHOD

Initially, the high-pressure injection and directional crystallization (HPIDC) technique has been specially developed by us for the fabrication of small diameter InSb wires. This technique is based on pressure injection of liquid material into a closed-end capillary with subsequent controllable crystal growth. In the sequel, this technique was used in our laboratory and other research institutes to grow the glass-coated wires of Bi, Sb, Bi$_{68}$Sb$_{12}$, Ge, PbTe and InSb-NiSb.

In our experiments we used the capillaries made of the commercial Pyrex and quartz glasses, which have a high chemical and thermal stability at temperatures below $T_s$. These capillaries were obtained by softening a piece of heavy-walled tubing inside an electrical furnace at $T \lesssim 800^\circ$C (Pyrex) or with a two-tip gas-oxygen burner at $T \lesssim 1300^\circ$C (quarts), and stretching it with a high speed. Depending on the glass viscosity and the pulling speed, long capillaries with different cross-section
dimensions can be obtained. We made the capillaries with a wall thickness of 5 - 15 μm, i.e., much smaller than the wall thickness of capillaries used by Gurvitch [8]. These capillaries were cut in lengths of about 20 cm long. After standard cleaning procedures, each capillary was closed at one end by glass softening, while the other capillary end remained open. The capillaries and the starting semiconducting material were placed inside a pressure cell made of a thick-walled quartz tube (Fig. 2). Each capillary was fixed at the closed end to a metallic plate jointed to a system of permanent magnets. This system is used to move the capillaries vertically.

A background pressure of ~ 10^{-3} Pa was achieved in the quartz cell before the melting of the parent semiconductor is initiated by the upward movement of a travelling hot furnace. The furnace temperature profile has a sharp bend at the sides. The temperature inside the furnace is stabilized by a commercial temperature controller, and a temperature stability better than 0.5°C over more than 24 hours was achieved. Once material becomes molten, the open ends of the capillaries are immersed into the melt to a depth of 5-10 mm. As a rule, the introduction of the capillary ends into the liquid material is the most difficult and laborious procedure in the HPIDC technique due to the surface tension of the melt and high flexibility of the thin glass capillaries. To ease this procedure, we have incorporated a generator of ultrasound waves into the design of the apparatus. For injection of liquid material into capillaries, an argon pressure of 6·10^5 Pa was used. Under such a pressure, about 90% of the capillaries with inside diameter larger than ~ 3 μm are filled all the way from the entrance to the closed end, the rest of the capillaries are filled partially. The same inert gas pressure was maintained during cooling back to room temperature.

![Fig.2. Sketch of the laboratory-scale apparatus for fabrication of thin glass-coated semiconducting wires using the HPIDC method.
1a, 1b - vacuum valves; 2 - metallic tube; 3 - quartz tube; 4 - permanent-magnet system to move capillaries; 5 - support for capillaries; 6 - glass capillaries; 7 - molten material; 8 - electric furnace; 9 - direction of furnace movement during wire crystallisation.

The crystallization of the glass-coated melted core was performed by the downward movement of the furnace at a speed, which can be changed from 0.4 to 5 cm/hour. In its downward movement,
the furnace creates a sharp temperature gradient (~ 50°C/cm) along the filled capillaries. Under such conditions, the nucleus of a melt-grown wire is initiated at the capillary tip, allowing for extra liquid material to flow out.

The glass coating was removed in a 20% hydrogen fluoride aqueous solution. The best wires grown by the HPIDC technique have extremely smooth and fine surfaces with no detail evident even in the scanning electron microscope. The wire diameters have ranged from thin (~3 µm) to very thick (~1 mm). Preliminary tests show that the smooth wires with micron diameters are mechanically strong, with yield points at greater than 1% strain at \( T = 300 \text{ K} \) as in the case of fine whiskers.

A closed inspection of the conventional HPI [8] technique shows that it contains an avoidable procedure of recovering the filled capillaries from solidified material. This time-consuming procedure is needed in the case when both ends of starting capillaries are open. In our improved version of the HPI technique, the procedure of chemical etching is eliminated by using the capillaries closed at one end. Besides, in the conventional HPI technique, the nucleation process is initiated by slow cooling the filled capillaries inside a furnace, where the crystallization of the melt proceeds from the side walls of the capillary or, at best, from both ends of the capillary. The design of our laboratory-scale apparatus (Fig. 2) permits to perform crystallization in a directed temperature gradient, where the wire growth takes place from the closed end of the capillary to the open one. In this case, the excess of the molten material, which appears as a result of expansion on crystallization, is pushed out of the capillary through the open end. Clearly, the application of unidirectional crystallization directly after the filling procedure is also effective in the generation of compositionally uniform wires. Besides, the HPIDC apparatus permits to utilize the reactive atmosphere processing, which greatly broaden the spectrum of materials to which this method is applicable.

Since the equipment used by us could sustain pressures only up to 6·10^5 Pa and we did not use any wetting agent, the smallest wire diameter that we obtained at the maximum operating pressure is about 3 µm for Bi and InSb. To fill capillaries with internal diameters ~0.1 µm, it is necessary to design an operating cell that can sustain pressures up to 150·10^5 Pa.

As we mentioned in Introduction, the HPI technique is widely used to produce bismuth wires embedded in porous anodic alumina having channel diameters from 20 to 200 nm. However, it is difficult to analyze numerous experimental data on the solidification of these Bi wires; they may not be systematized, because the kinetics of solidification is highly sensitive to the presence of impurities, which may serve as nucleation centers. Huber et al. [10] found Cu and Al impurities in their Bi nanowire arrays after processing. To increase the filling factor, Zhang et al. [9] introduced intentionally Cu impurities into liquid Bi in order to decrease the surface tension, which has a high value in the case of pure Bi (~380 dyn/cm at 271°C); as a consequence, only a small amount of the channels can be filled. These impurities are known to form non-uniform microstructures due to their segregation during Bi solidification. Apart from foreign substances, inclusions of a stress-induced high-pressure phase of Bi have been detected inside the porous alumina template [9]. The physical properties of these impure and/or two-phase wires may be very different from those of pure monophase Bi wires. In a very thin wire, even a single planar defect or heterogeneous nanocluster may modify the electronic transport properties non-trivially although the averaged lattice parameters are maintained. It is to be noted here that the quantum size effects can be observed only in compositionally uniform wires with sufficiently perfect crystal structure. This can be explained by the fact that the broadening of energy levels upon size quantization, caused by the scattering of carriers on various impurities, should be small in comparison with the gap between the levels. Therefore, the search for new methods of fabrication of wires having a perfect microstructure and geometry is of significance for the developing of nanowire electronics.

CONCLUSIONS

The melt spinning of semimetallic and semiconducting materials with Pyrex glass was investigated as a means of producing long wires with good structural parameters. This method requires for its successful realization to use only conducting materials. Continuous Bi wires with diameters
from 100 nm to about 10 µm were obtained from the molten state at ~ 900 - 1000°C using winding speeds from 1 to several 10 m/s. As we have previously shown [23], the samples of these wires 2-7 mm in length have as high zero-magnetic-field resistances, as large values of transverse magnetoresistance at 300, 77 and 4.2 K and can be potentially used as sensitive magnetoresistive elements for wide-range field-sensing devices. However, the GCMS method involves the high operating temperatures, ultrarapid quenching rates and crystallization in a restricted space, which causes the appearance of numerous structural defects and impurities that markedly deteriorate the transport properties of as-drawn wires (for example, achieving of ballistic transport in structures made of these wires becomes problematic). Since Bi expands 3.1 % upon crystallization, the glass-coated Bi wires with submicron diameters may be under residual radial and axial compressive strains. Moreover, this method is practically inapplicable for preparation of long, compositionally uniform wires of the most semiconducting materials of industrial importance, such as InSb, PbTe, etc.

A new approach to the fabrication of semiconducting wires was proposed. The general concept of the proposed HPIDC method is that molten material is injected into a pre-evacuated glass capillary closed at one end and unidirectional solidification occurs along the capillary axis from the closed to open end. As a result, the excess of the molten material, which appears due to expansion on crystallization, is pressed out of the capillary through its open end and this permits to eliminate the appearance of high compressive pressures, which usually are responsible for the phase inhomogeneity and the great number of defects. The HPIDC method has some other advantages over traditional Taylor and GCMS techniques used for the wire fabrication. It allows one to utilize operating temperatures close to the melting temperature of the required material; to produce wires with different diameters under the same preparation conditions; to ensure high structural perfection of fabricated wires because these wires are obtained as final products after equilibrium crystallization. Also, this method does not require further processing (mechanical and/or chemical) as in the case of ordinary HPI technique. By this technique, it is possible to produce thin wires not only of InSb, Bi, Sb and Bi₈₈Sb₁₂, but also from materials that greatly contract under solidification such as PbTe. However, using our present pressure cell, we were unable to obtain wires with diameters smaller than ~ 3 µm.

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