Filiform nanoarchitectures consisting of arrays of highly integrated Bi nanowires in glass envelopes

V. POSTOLACHE[1], A. IOISHER[2], E. MONAICO[1], E. BADINTER[2], I.M. TIGINYANU[1,3]
[1] *National Center for Materials Study and Testing, Technical University of Moldova, Chisinau MD-2004, Moldova*
[2] *ELIRI Research Institute, Chisinau MD-2045, Moldova*
[3] *Institute of Electrical Engineering and Industrial Technologies, Academy of Sciences of Moldova, Chisinau MD-2028, Moldova*

Abstract **— Using a modified version of the Taylor method, we show the possibility to produce glass micro-cables comprising huge amounts of Bi nanowires in glass envelopes, each nanowire being electrically isolated from the neighbouring ones. Besides, we present technological routs for the fabrication of micro-cables exhibiting filiform nanoarchitectures within domains. Etching of micro-cables in aqueous solution of HF reveals the catalytic role of bismuth. We succeeded to fabricate Ohmic contacts to arrays of Bi nanowires integrated in glass micro-cables and to measure the temperature dependence of their electrical resistance.**

Index Terms **— Bi nanowires, filiform nanoarchitecture, glass micro-cables, etching, Ohmic contacts.**

INTRODUCTION

Bismuth has a rhombohedral structure with a low melting point of 271.4°C. Bulk bismuth is a semi-metal, while in wire form with a diameter smaller than 50 nm Bi exhibits semiconductor properties [1]. Over the last years, there has been increasing interest in Bi nanowires due to their promising thermoelectric properties. The electronic band gap of a bismuth wire proves to be a function of its diameter, varying from 0 eV at 50 nm to 0.7 eV at 5 nm. Arrays of bismuth micro- and nanowires were produced previously [2-10] by using templated electrochemical deposition, pressure injection of molten Bi, or by infiltrating and condensing bismuth vapour into the nanochannels of porous alumina or glass templates. Note that templated approaches allow one to fabricate arrays of micro-nanowires with the length up to several hundreds of micrometers or, under specific conditions, up to one millimeter or so. In this work, using the technology proposed previously [11], we demonstrate the possibility to fabricate glass micro-cables with diameters of several hundreds of micrometers and length up to tens of centimeters, comprising arrays of Bi nanowires, each nanowire being electrically isolated from neighbouring ones.

EXPERIMENTAL

The developed technological route consists of several steps. The first step is known as Ulitovsky approach [12] and it comprises (a) levitation melting in an applied high-frequency electromagnetic induction field of a certain amount of metal, semimetal or semiconductor material placed in a glass tube, (b) heating-induced softening of the bottom end of the glass tube holding a drop of the conducting material, (c) capillary drawing from the lower end of the glass tube resulting in the formation of metal, semimetal or semiconductor micro- or nanowire in glass envelope, and (d) cooling of the micro- or nanowire in glass envelope to reach crystallization of the core material and solidification of the glass coat.

The second step comprises (a) assembling of individual microwires in a bunch covered by a shared glass coat, and (b) stretching of the bunch under proper heating conditions providing melting and repeated crystallization of the conducting cores with their simultaneous thinning up to a few tens of nanometers in diameters. The second step can be repeated several times until desired diameter of metal, semimetal or semiconductor nanowires is reached. As a result we obtained glass micro-cables or filiform nanoarchitechtures consisting of tens and even hundreds of thousands of metal, semimetal or semiconductor nanowires embedded in individual glass envelopes. The scheme of thinning of microwire bunch (workpiece) is illustrated in Fig.1. To simplify the technological equipment, the heating of the workpiece is carried out within the hollow cylinder heated by high frequency.

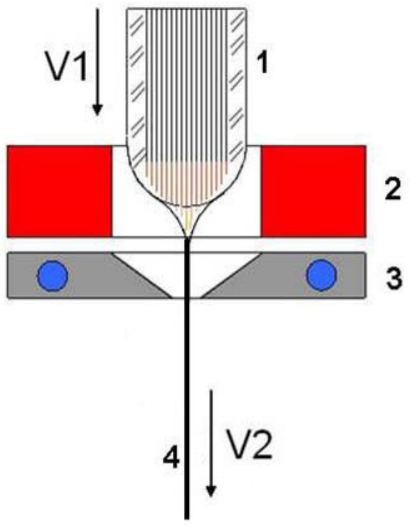

Figure 1. The scheme of thinning of microwire bunch: 1 – microwire bunch; 2 – heated hollow cylinder; 3 – high frequency inductor; 4 - bunch of nanowires (filiform nanocomposition).

The third step usually comprises (a) assembling plenty of above mentioned filiform nanocompositions (regarding them in this case as workpieces) in a common bundle covered by a shared glass coat, and stretching of the bundle under relevant heating conditions as described above. In this case a domain structure of the micro-cable is assured. Below we will demonstrate the possibilities of the technology involved in regard to integration of Bi nanowires in glass micro-cables.

To study the homogeneity of Bi nanowires along the bunch, we subjected the micro-cables to etching in 20 % HF solution in water at room temperature. After etching the samples were treated in 20 % KOH solution at 40°C with subsequent cleaning in distilled H_2O at room temperature. A TESCAN scanning electron microscope (SEM) equipped with an Oxford instruments INCA energy dispersive X-ray (EDX) system was used to study the morphology and chemical composition of the samples. To explore the electrical resistance of Bi filiform nanoarchtechtures, we fabricated Ga/In alloy contacts which exhibited good characteristics in a wide temperature interval (23-270 K). A Keithley 2400 instrument was used to study the resistance as a function of temperature, the sample being mounted on the cold station of an ARS closed cycle cryostat system.

III. RESULTS AND DISCUSSION

Fig. 2 shows a bunch of Bi nanowires in glass envelopes assembled according to the scheme described above.

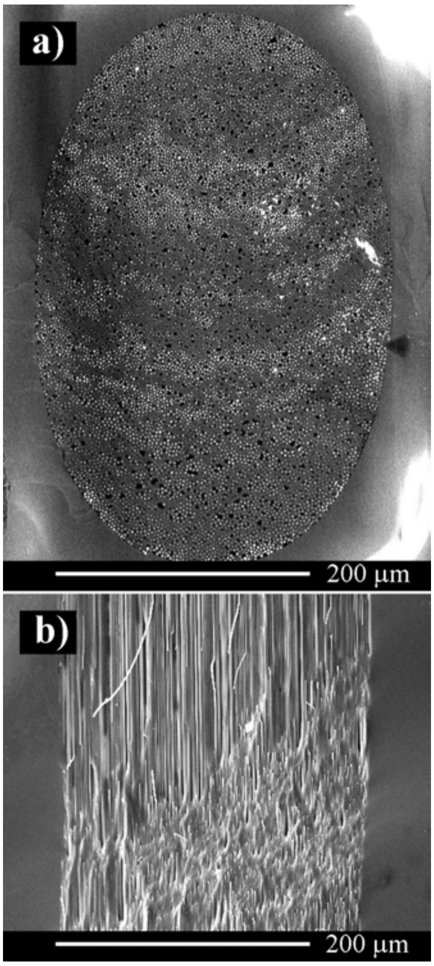

Figure 2. Morphology of the filiform nanoarchitecture in two cross-sections made perpendicular (a) and along (b) the micro-cable.

The bunch was subjected to stretching under proper heating conditions to assure melting and repeated crystallization of the Bi cores with their simultaneous thinning up. As a result we obtained a filiform nanoarchitechture consisting of a huge amount of Bi nanowires in glass envelopes.

Fig. 2 illustrates the morphology of the filiform nanoarchitecture in two cross-sections made perpendicular (a) and along (b) the micro-cable. One can see that the Bi nanowires are confined in an ellipse like region. Note that each of Bi nanowires has its own glass envelope. Besides, the bunch of nanowires shares a common glass coat. The length of the obtained micro-cables may be as high as several tens of centimeters.

The result of etching of micro-cables in aqueous solution of HF for 3 and 30 min is illustrated in Fig. 3. It is interesting to note that glass etching starts in regions neighbouring to Bi nanowires, i.e. Bi plays the role of catalyst. The outer common coat remains practically intact in comparison with the filiform nanoarchitecture confined in the central part of the micro-cable.

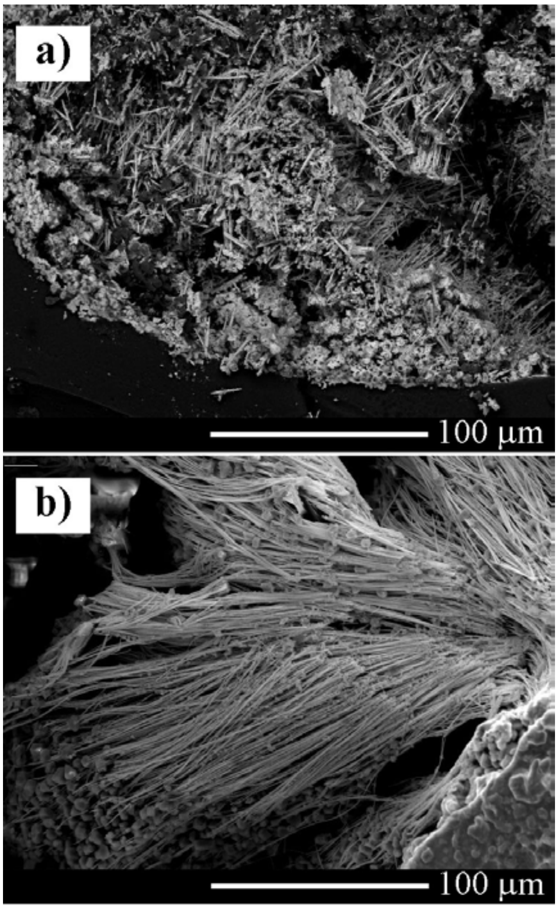

Figure 3. Morphology of the micro-cable after etching in aqueous solution of HF for 3 min (a) and 30 min (b).

We succeeded also to fabricate micro-cables exhibiting filiform nanoarchitectures within domains. In this case many bunches were assembled in a single bundle with a common glass coat, see Fig. 4. Note that the treatment procedures do not eliminate completely the free spaces between bunches and in most cases some triangular or rectangular voids are observed within the central part of the micro-cable. Etching in HF aqueous solution attacks the domains comprising filiform nanoarchitectures, the glass areas between domains remaining practically intact (see the left insert in Fig. 4). This confirms our suggestion that bismuth plays the role of catalyst. After etching for 30 min one can distinguish bunches of relatively long Bi nanowires with the diameter of about 300 nm, see the right insert in Fig. 4.

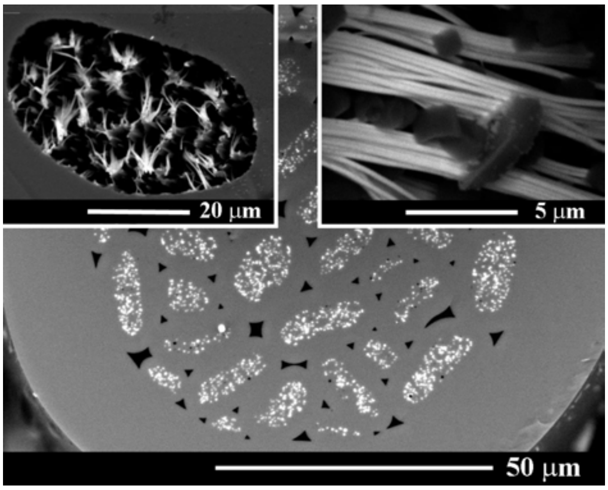

Figure 4. Micro-cable exhibiting filiform nanoarchitectures within domains. The inserts show the morphology of a domain after etching for 3 min (left insert) and 30 min (right insert).

The analysis of the chemical composition carried out by help of the techniques of energy dispersive X-ray analysis confirms that the filiform nanoarchitectures consist of bismuth and glass. According to the data presented in Fig. 5, the content of chemical elements in atomic percents is as follows: Bismuth – 0.68, Silicon – 33.15, and Oxygen – 66.17.

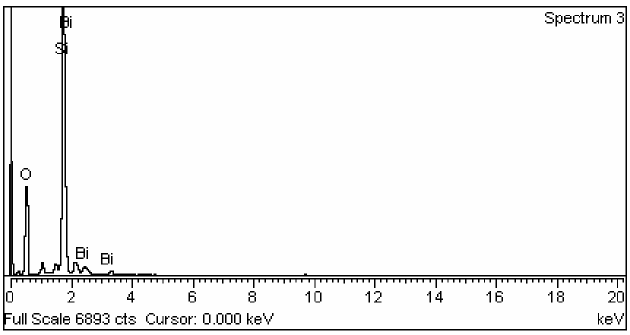

Figure 5. The result of EDX-analysis of chemical composition of filiform nanoarchitecture.

The Ga/In electrical contacts to the array of Bi nanowires prove to exhibit linear volt-ampere characteristics in the temperature interval from 23 to 270 K (Fig. 6). At the same time we found that at room temperature the used Ga/In alloy does not provide linear volt-ampere characteristics. In our opinion this can be related to the fact that the In/Ga alloy is in liquid phase at 300 K and it solidifies at temperatures as low as a few degrees Centigrade.

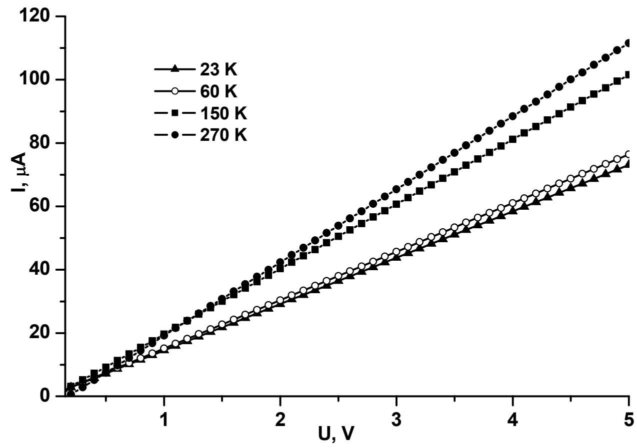

Figure 6. Volt-ampere characteristics at different temperatures of Ga/In electrical contacts to arrays of Bi nanowires in glass envelope.

As expected, the temperature dependence of resistance demonstrates the metal properties of bismuth nanowires with the diameter of about 300 nm (Fig. 7). One can mention in this regard that metal to semiconductor transition occurs in Bi nanowires with diameters lower than 50 nm.

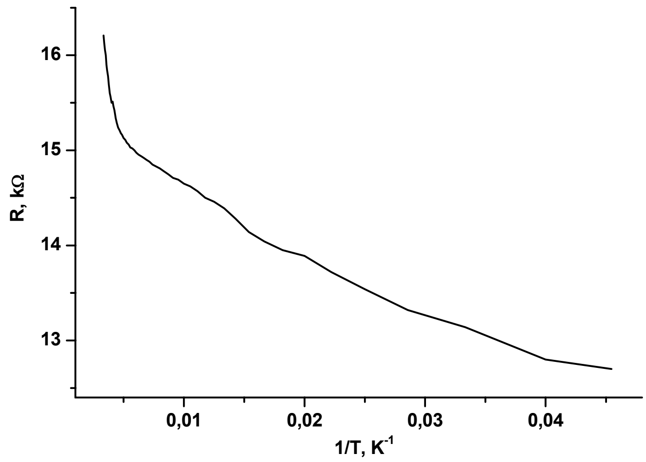

Figure 7. Temperature dependence of resistance of a bunch of Bi nanowires in glass envelopes.

IV. CONCLUSION

We demonstrated the possibility to integrate huge amounts of Bi nanowires in a single glass micro-cable by using a modified version of the Ulitovsky method. Integration of many micro-cables was shown to lead to the observation of filiform nanoarchitectures within domains. The chemical composition analysis based on EDX confirmed the presence of bismuth, silicon and oxygen. As a result of systematic investigations of wet etching in aqueous solution of HF, the catalytic property of Bi nanowires was evidenced. Ga/In Ohmic contacts were elaborated to arrays of Bi nanowires in glass envelopes and the temperature dependence of their electrical resistance was found to be similar to that inherent to metals.

ACKNOWLEDGMENT

This work was supported by the Supreme Council for Research and Technological Development of the Academy of Sciences of Moldova under Grant no 06.02.90870.

REFERENCES

[1] A. Boukai, K. Xu, J.R. Heath, Advanced Materials 18, 864 (2006).
[2] K. Liu, C.L. Chien, P.C. Searson, Y.Z. Kui, Appl. Phys. Lett. 73, 1436 (1998).
[3] K.M. Hong, F.Y. Yang, K. Liu, D.H. Reich, P.C. Searson, C.L. Chien, F.F. Balakirev, G.S. Boebinger, J. Appl. Phys. 85, 6184 (1999).
[4] Liang Li, Young Zhang, Guanghai Li, Lide Zhang, Chem. Phys. Lett., 378 (2003).
[5] Feng Xiao, Carlos Hangarter, Bongyoung Yoo, Youngwoo Rheem, Kyu-Hwan Lee, Nosang V. Myung, Electrochimica Acta 53, 8103 (2008).
[6] Z. Zhang, X. Sun, M.S. Dresselhaus, J. Ying, Appl. Phys. Lett., 73, 1589 (1998).
[7] J. Heremans, C.M. Thrush, Y.M. Lin, S. Cronin, Z. Zhang, M.S. Dresselhaus, J.F. Mansfield, Phys. Rev. B 61, 2921 (2000).
[8] T.E. Huber, P. Constant, M.J. Graf, C.A. Foss, J. Mater. Res. 15, 1816 (2000).
[9] Ya. Hasegawa, Yo. Ishikawa, H. Morita, T. Komine, H. Shirai, H. Nakamura. J. Appl. Phys. 97, 083907 (2005).
[10] Ya. Hasegawa, M. Murata, D. Nakamura, T. Komine, T. Taguchi, Sh. Nakamura. J. Electron. Mater. 38, 944 (2009).
[11] Ioişer A. Nanostructure and process for manufacture thereof. Patent of Republic of Moldova. Nr. 2510, 18.02.2003.
[12] E. Ia. Badinter, N. R. Berman, I. F. Drabenco, V. I. Zaborovski, Z. I. Zelikovski, and V. G. Cheban, Cast Microwire and Its properties (Shtinitsa, Kishinev, 1973), pp. 6–196.