

**INTEGRATION OF Ge NANOWIRE ARRAYS IN GLASS MICRO-FIBERS**

**A. Ioisher<sup>\*</sup>, E. Badinter<sup>\*</sup>, E. Monaico<sup>\*\*</sup>, V. Postolache<sup>\*\*</sup>, H.L. Hartnagel<sup>\*\*\*</sup>,  
N. Leporda<sup>\*\*\*\*</sup>, I. Tiginyanu<sup>\*\*\*\*</sup>**

<sup>\*</sup> *ELIRI Research Institute, Miron Costin str. 5, Chisinau MD-2045, Moldova*

<sup>\*\*</sup> *National Center for Materials Study and Testing, Technical University of Moldova,  
Bd. Stefan cel Mare 168, Chisinau MD-2004, Moldova,*

<sup>\*\*\*</sup> *Institute for High Frequency Electronics, Technical University Darmstadt,  
Darmstadt D-64283, Germany,*

<sup>\*\*\*\*</sup> *Laboratory of Nanotechnology, Institute of Electronic Engineering and Nanotechnologies,  
Academy of Sciences of Moldova, Academy str. 3/3, Chisinau, MD-2028 Moldova,  
[tiginyanu@asm.md](mailto:tiginyanu@asm.md)*

**Introduction**

Over the last decade, Germanium has experienced renewed interest for a wide spectrum of applications. This interest is caused by a number of properties that are superior to those of Si, e.g., higher carrier mobility, larger exciton radius and hence stronger quantum confinement in low-dimensional structures, and the prospect of lower processing temperatures and thus easier integration in complex electronic systems. In particular, Ge nanowires offer unique opportunities for the development of high-performance field-effect transistors [1], photodetectors [2], sensors for biological and chemical species [3], waveguides [4] etc. Due to its high refractive index, Ge is a very promising material for photonic applications. Note that a single Ge nanowire, introduced into a hole adjacent to a photonic crystal fiber, causes strong polarization dependent loss in the visible spectral region, which could be used as an effective in-fiber polarizer [5].

Ge nanowires were successfully produced using various methods such as vapor-solid-solid synthesis [6], gold nanocrystal seeded supercritical fluid-liquid-solid synthesis [7, 8], low-temperature thermal evaporation [9], electron beam evaporation [10] etc. Large arrays of Ge nanowires were fabricated by templated electrochemical deposition [11] and electrochemical etching of bulk Ge substrates [12]. Although most of these methods offer possibilities to control the diameter of nanowires, there is a length limitation which usually does not exceed a few hundreds of micrometers. Recently we succeeded in integration of huge amounts of electrically isolated metal and semimetal nanowires in glass fibers (named Filiform Nanostructures – FNS) with the diameter of up to a few hundreds of micrometers [13, 14]. In this communication, we report on a technological route allowing record integration of electrically isolated Ge nanowires in a human-hair-like glass micro-fiber, the length of the micro-fiber reaching one meter.

**Fabrication**

The first step of the proposed technological route is based on the well-known approach of filling in with conductive melt of a glass capillary drawn from a glass tube [15]. In our experiments, a few grams of Ge were inserted into a glass tube with the internal diameter ranging from 8 to 12 mm, and the tube wall thickness of 0.8 to 1.2 mm, see Fig. 1,*a*. We selected a compatible glass to provide a minimum value of the interfacial tension between the glass and the melt in the micro-bath representing glass coating flowing around the suspended molten Ge drop, at the same time no chemical reactions should occur at the interface. Note that the melting temperature  $T_m$  for Ge equals 937 °C.

The microwires produced by us are characterized by a conducting core diameter ranging from 1 to 12  $\mu\text{m}$  and a glass coating thickness of 5 to 20  $\mu\text{m}$ , the length reaching dimensions as high as one kilometer. Densely packed bundles were mechanically assembled from equal-length cut initial microwire pieces (10 to 20 cm long) and inserted in a joint glass tube closed at one end and having internal diameter of 3 to 6 mm and wall thickness of 1 to 2 mm, see Fig. 1,*b*. The total number of pieces in one bundle usually does not exceed 30,000. Note that the thermal expansion coefficient of the encircling joint glass tube should be close to the effective expansion coefficient of the bundle. High-density packaging of the microwire pieces resulting in their two-dimensional hexagonal distribution is provided by pumping-down to vacuum as low as  $10^{-3}$  Pa with simultaneous temperature increase up to the temperature of glass softening.

To subject the obtained preform to stretching, the top end of it is fixed at the feeding mechanism controlling the downward movement, while the bottom part is placed in a tubular heater, see Fig. 1,c. When the core of the microwire pieces represents brittle materials like Ge, the tubular heater should provide bundle heating up to the glass softening and melting of the microwire cores. The shape of the stretching part of the preform is cone-like with the height  $h$  depending upon the concrete technological conditions.

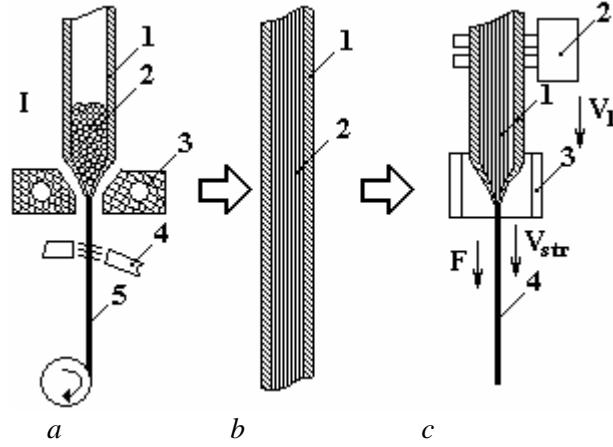


Fig. 1. Schematic illustration of the main steps of the proposed technological route. (a) formation of semiconductor microwire in glass insulation by capillary drawing from the bottom of a glass tube softened by a conducting melt drop levitating in the high-frequency electromagnetic induction field: 1 – glass tube; 2 – molten semiconductor; 3 – high-frequency inductor; 4 – liquid jet; 5 – glass-encapsulated microwire; (b) mechanical assembly of a bundle from equal-length cut glass-encapsulated Ge microwires: 1 – joint glass tube; 2 – densely packed bundle of semiconductor microwires in glass insulation; (c) stretching of the obtained preform under proper heating conditions to reduce the diameters of the stacked together microwires down to a few hundreds of nanometers: 1 – preform subjected to stretching; 2 – feeding mechanism controlling the downward movement of the preform at the rate  $v_1$ ; 3 – tubular heater; 4 – stretched bundle of micro- or nanowires in glass insulation

The process of preform thinning is realized in several cycles. The scaling ratio  $k_i$  for the reduction of the preform diameter varies from cycle to cycle, therefore the total thinning  $K$  of the preform subjected to  $n$  stretching cycles (usually  $1 < n < 6$ ) and its final diameter  $D$  are determined by the relations  $K = k_1 \cdot k_2 \cdot \dots \cdot k_n$  and  $D = D_0/K$ , where  $D_0$  is the initial diameter of the preform.

Stretching of preforms consisting of glass micro/nanofibers with molten semiconductor cores should be realized at maximum possible glass viscosity, i.e. at lowest possible temperature still assuring that the core component is in liquid phase and simultaneously providing conditions for thinning of the glass micro/nanofibers by a factor of two to three during one technological cycle. We found that such a situation is easily realized in preforms comprising micro/nanowires of metals/semimetals (e.g. Pb/Sn, Bi) crystallizing at temperatures lower than the temperature of glass solidification. However, when the core material crystallizes before the glass solidification during the thinning process, as happens in Ge, the forces of viscous glass stretching may cause mechanical ruptures in the solidified crystalline core. To avoid occurrence of ruptures, it is important to use high temperature glasses, e.g. vycor, that exhibit enough viscosity during core solidification. An alternative solution is to decrease the tensile force so that the tension in the crystallized core remains below the ultimate strength, although this leads to considerable decrease in the stretching rate.

When fabrication of the filiform nanostructures involves melting of the core material (as happens in the case of Ge), the ratio between preform tensile force  $F$  and dynamic viscosity  $\eta_g$  of the glass is determined by the following semi-empirical formula, obtained taking into account the rheological character of the flow in the stretching cone-like part of the preform:

$$\frac{F}{\eta_g} = C \frac{(v_{str} - v_1)}{h} [D_E^2 - D_I^2(1 - \chi) - d^2 N \chi] \quad (1)$$

where  $v_1$  is the rate of downward movement of the preform,  $v_{str}$  is the stretching rate,  $h$  is the height of the preform heating/softening zone,  $D_E$  and  $D_I$  are external and internal diameters of the encircling glass tube,  $d$  is the average diameter of the semiconductor cores in the initial or intermediate preforms,  $N$  is the number of

micro/nanowires in the preform,  $\chi$  is the filling coefficient of the preform volume (usually  $0.7 < \chi < 0.9$ ),  $C$  is dimensionless empirical coefficient depending upon the characteristics of the experimental set-up for stretching ( $700 \leq C \leq 1300$ ). Proceeding from the preform architecture and glass viscosity  $\eta_g$  determined by the temperature in the cylindrical furnace, one can calculate by Eq. 1 the tensile force  $F$  required for the preform stretching at any cycle of thinning.

To provide continuity of the semiconductor cores in the filiform nanostructures, the main parameters, including surface tension  $\sigma_m$  of the core material, tensile force  $F$  and glass viscosity  $\eta_g$  should satisfy the following empirical inequality

$$A \leq \frac{\eta_g v_{str}}{\sigma_m} \frac{|D_E^2 - D_I^2(1-\chi) - d^2 N \chi|}{Nd^2} + \frac{F}{h\sigma_m} \frac{Nd^2}{[D_E^2 - D_I^2(1-\chi) - d^2 N \chi]} \leq B \quad (2)$$

where the dimensionless lower bound  $A$  determines the conditions for the suppression of the formation of semiconductor micro/nanodrops leading to the emergence of ruptures, while the dimensionless upper bound  $B$  is related to the ultimate strength of the filiform nanostructure at glass viscosity as high as  $\eta_g \sim 10^5$  kg/(m·s). The inequality (2) shows that it is the increase in the preform tensile force  $F$  and glass viscosity  $\eta_g$  that withstands the destruction-oriented influence of the surface tension  $\sigma_m$  of the molten core material. According to the results of our study, the values of  $A$  and  $B$  equal 40 and  $1.5 \times 10^3$  respectively. Note that expressions (1) and (2) impose restrictions on the viscosity of the glass components of the filiform nanostructure, the optimum values of which range over the interval from  $3 \cdot 10^4$  to  $2 \cdot 10^5$  kg/(m·s).

### Results of characterization

The morphology of Ge NWs was studied at VEGA TESCAN TS 5130MM Scanning Electron Microscope (SEM) equipped with an Oxford Instruments INCA energy-dispersive x-ray (EDX) system. Raman scattering from Ge filiform nanostructures was measured at room temperature with a Horiba Jobin Yvon LabRam IR system in a backscattering configuration. The 632.8 nm line of a He-Ne laser was used for off-resonance excitation with less than 4 mW power at the sample.

Fig. 2,*a,b* illustrates SEM images taken in longitudinal and cross sections from a bundle of glass-encapsulated crystalline Ge nanowires encircled by a joint glass envelop and subjected to stretching. As one can see from Fig. 2,*b*, the cross-sectional view exhibits a two-dimensional quasi-ordered hexagonal distribution of Ge nanowires, some of them getting out from the glass envelop. The average diameter of Ge nanowires equals 150 nm, while their length is determined by the length of the glass micro-fiber after stretching which reaches dimensions as high as 1 m.

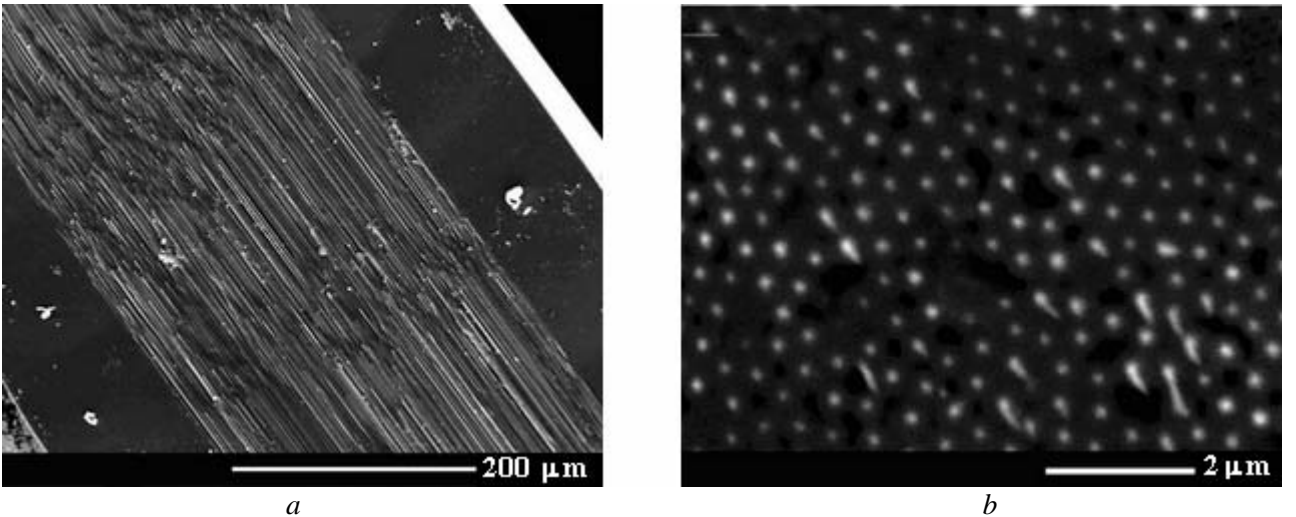


Fig. 2. SEM image in longitudinal (a) and cross (b) sections taken from a densely packed bundle of glass-encapsulated Ge NWs after stretching

The micro-Raman scattering was studied from a cross-section of the micro-fiber, focusing the laser radiation on an area where some Ga nanowires got out from the glass envelope. The first-order Ge-Ge optical phonon mode was found at  $297.9 \text{ cm}^{-1}$ , the full width at half maximum of the micro-Raman scattering peak being equal to  $8 \text{ cm}^{-1}$  (Fig. 3). The observed downward shift of the Ge optical phonon frequency with respect to its value in bulk crystalline Ge ( $300 \text{ cm}^{-1}$  [16]) reflects the existence in Ge

nanowires of tensile stress caused by the difference in thermal expansion coefficients of germanium and glass.

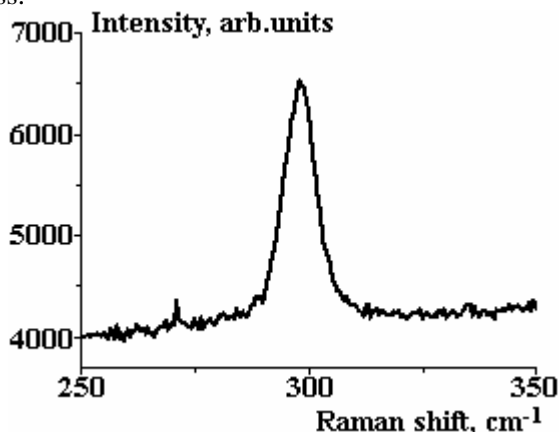


Fig. 3. Micro-Raman scattering spectrum taken from a bundle of glass-encapsulated Ge NWs at 300 K

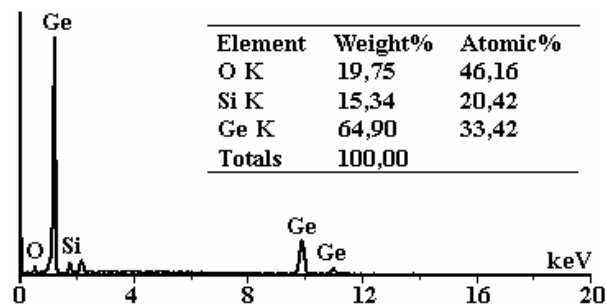


Fig. 4. EDX analysis of the chemical composition of Ge nanowire array integrated in glass micro-fiber

The analysis of the chemical composition carried out by EDX techniques confirms that the filiform nanostructure consists of Ge and glass (Fig. 4). It is also possible that the Ge NWs are covered by a thin layer of native oxide, i.e. GeO<sub>2</sub>. To clarify this issue additional investigations are needed.

### Conclusion

The proposed technological route allowed us to fabricate meter-long human-hair-like glass micro-fibers (named FNS) comprising tens of thousands of Ge nanowires. We reached high integration of nanowires with diameters as low as 150 nm, all integrated Ge nanowires being electrically isolated from each other. The obtained results are indicative of new challenges for the elaboration of photonic crystals and negative index metamaterials based on two-dimensional dielectric periodic and quasi-periodic structures. Also quantum-electronic logic systems can be envisaged.

### Acknowledgement

This work was supported by the Supreme Council for Research and Technological Development of the Academy of Sciences of Moldova under the State Programme “Nanotechnologies and Nanomaterials”, Grant # 09.836.05.03A.

### REFERENCES

- Xiang J., Lu W., Hu Y., Wu Y., Yan H., Lieber C.M. Ge/Si nanowire heterostructures as high-performance field-effect transistors. *Nature*. 2006, **441**, 489–493.
- Chueh Y-L., Fan Z., Takei, K., Ko H., Kapadia R. Black Ge Based on Crystalline/Amorphous Core/Shell Nanoneedle Arrays. *Nano Lett.* 2010, **10**(2), 520–523.
- Cui Y., Wei Q., Park H., Lieber C.M. Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species. *Science*. 2001, **293**, 1289–1292.
- Kim Y., Song M.S., Kim Y.D., Jung J.H. Epitaxial Germanium Nanowires on GaAs Grown by Chemical Vapor Deposition. *J. Korean Phys. Soc.* 2007, **51**, 120–124.
- Schmidt M.A., Tyagi, H., Prill Sempere L., Russell P.S. Polarization Properties of PCF with Ge-Nanowire. *J Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science Conference and Photonic Applications Systems Technologies*, OSA Technical Digest (Optical Society of America, 2008), paper CFO4.
- Lensch-Falk J.L., Hemesath E.R., Lopez F.J., Lauhon, L.J. Vapor–Solid–Solid Synthesis of Ge Nanowires from Vapor-Phase-Deposited Manganese Germanide Seeds. *J. Am. Chem. Soc.* 2007, **129**, 10670–10671.
- Hanrath T., Korgel B.A. Supercritical Fluid–Liquid–Solid (SFLS) Synthesis of Si and Ge Nanowires Seeded by Colloidal Metal Nanocrystals. *Adv. Mater.* 2003, **15**, 437–440.
- Buriak, J.M. Organometallic Chemistry on Silicon and Germanium Surfaces. *Chem. Rev.* 2002, **102**, 1271–1309.
- Sutter E., Ozturk B., Sutter P. Selective growth of Ge nanowires by low-temperature thermal evaporation. *Nanotechnology*. 2008, **19**, 435607.
- Pecora E.M., Irrera A., Artoni P., Boninelli S.B. Heteroepitaxial Growth and Faceting of Ge Nanowires on Si(111) by Electron-Beam Evaporation. *Electrochem. Sol.-St. Lett.* 2010, **13**, K53–55.

11. Al-Salman R., Mallet, J., Molinari, M., Fricoteaux, P., Martineau, F. Template assisted electrodeposition of germanium and silicon nanowires in an ionic liquid. *Phys. Chem. Chem. Phys.* 2008, **10**, 6233–6237.
12. Fang C., Föll H. Carstensen J. Long Germanium Nanowires Prepared by Electrochemical Etching. *Nano Lett.* 2006, **6**, 1578–1580.
13. Badinter E., Ioisher A., Monaico E., Postolache V. and Tiginyanu I.M. Exceptional Integration of Metal or Semimetal Nanowires in Human-Hair-Like Glass Fiber. *Materials Letters.* 2010, **64**, 1902–1904.
14. MD 4046 B1 2010.05.31 Ioisher A., (MD), Badinter E., (MD), Tiginyanu I., (MD). *Method of Filiform Nanostructures Fabrication.*
15. Donald I.W. Production, properties and applications of microwire and related products. *J. Mater. Sci.* 1987, **22**, 2661–2679.
16. Kartopu, G.; Sapelkin, A.V.; Karavanskii, V.A.; Serincan, U.; Turan, R. Structural and optical properties of porous nanocrystalline Ge. *J. Appl. Phys.* 2008, **103**, 113518.

Received 14.12.10

### Summary

We report on a technological route for the integration of large arrays of Ge nanowires (NWs) in a human-hair-like glass micro-fiber, the length of the micro-fiber reaching one meter. The route comprises (a) the formation of semiconductor microwire in glass insulation by capillary drawing from the bottom of a glass tube softened by a conducting Ge melt drop levitating in the high-frequency electromagnetic induction field; (b) mechanical assembly of a bundle from equal-length cut microwires which are distributed in a two-dimensional quasi-hexagonal densely packed lattice encircled by a joint glass envelope; (c) stretching of the obtained preform under proper heating conditions to reduce the diameters of the stacked together microwires; (d) repeating the cut-assembly-stretching processes for the purpose of further decreasing in transverse dimensions of constituents down to 150 nm. The fascinating incorporation of huge amounts of Ge nanowires in glass micro-fibers opens new possibilities for the development of highly integrated photonic and quantum-electronic systems.

---