PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 19, № 1 (2018) P. 14-20
DOI: 10.15330/pcss.19.1.14-20

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 19, № 1 (2018) С. 14-20

PACS: 621.315.592

ISSN 1729-4428

Yu.V. Pavlovskyy[1], G. Luka[2], I.P. Ostrovskyy[3], N.T. Pavlovska[4]

Structure and Magnetic Properties of $Si_{0,97}Ge_{0,03}$ Whiskers

[1]*Ivan Franko Drohobych State Pedagogical University, 24, Franko Str., 82100 Drohobych, Ukraine, yu_pavlovskyy@ukr.net*
[2]*Institute of Physics, Polish Acad. of Sciences, al. Lotników 32/46, 02-668 Warsaw, Poland*
[3]*Lviv Polytechnic National University, S. Bandera Str., 12, 79013, Lviv, Ukraine*
[4]*Drogobych Comprehensive School I-III degrees №4, Stryiska Str., 28, 82100, Drohobych, Ukraine*

By the method of chemical transport reactions in the closed halogen system Si-Au-Pt-B-Br, whiskers Si1-xGex x = 0.01-0.08 of transverse dimensions 0.1-100 μm were grown. Structural and magnetic properties of the obtained crystals are investigated. The method of scanning electron microscopy showeds that on the surface of needle-like crystals, with transverse dimensions of 50-80 microns, a porous shell with a thickness of 50-60 nm is present. From the analysis of the energy spectra of X-rays, it was found that the surface shell contains significant concentration atoms of oxygen and of carbon. In turn, oxygen and carbon peaks were not detected on the inner layers of samples. It has been established that the chemical etching of the surface layer of crystals leads to the improvement of their structural and magnetic properties.

Key words: whiskers of silicon-germanium, electron microscopy, X-ray spectrum, magnetic susceptibility.

Article acted received 29.12.2017; accepted for publication 05.03.2018.

Introduction

The whiskers due to its unique shape, size, high elasticity and mechanical strength, which is explained by structural perfection, are increasingly used in various fields of human practice (aviation, rocket and space, medical, transport, telecommunications, etc.). Various devices of micro- and nanosystem technique have been made based on the whiskers, for example, high sensitive sensors of residual concentrations of various gases and liquids [1-3], temperature sensors [4, 5], gauges for measuring mechanical characteristics, sensors of various physical quantities, superstrong composite materials, miniature suspension devices, microprobes [6-11], etc. One of the prospect directions of the whisker application is their use in chemical and biological sensors [12-14]. The whiskers are excellent objects for physical research, since they allow to vary the perfection of the crystal structure within wide limits and, therefore, simulate different conditions for verifying the correctness of theoretical calculations to refine existing models, and obtain new data on the physical nature of various processes occurring in solids.

Nowadays the greatest attention is paid to the study of Si, Ge whiskers and their solid solution $Si_{1-x}Ge_x$ due to the simplicity of the technological process of their preparation, the low cost of raw materials, a wide range of practical applications and the ability of devices to work in a wide range of temperatures. The authors of the works [15-17] revealed the peculiarities of the structural, magnetic and micromechanical properties of filamentary crystals, however their physical nature was not fully elucidated. Therefore, the purpose of this work was to find out the features of the structure of $Si_{1-x}Ge_x$ whiskers and its influence on their magnetic properties on the basis of studying the results of scanning electron microscopy, X-ray radiation energy spectrum as well as magnetic susceptibility.

I. Experimental results and their discussion

The Si-Ge whiskers were grown by the method of chemical transport reactions in a closed bromide system using doping impurities (Pt, B, Au) [15]. The content of germanium in Si-Ge solid solution was controlled by the microprobe analysis and was x = 0.03. As is known, when changing from needle crystals to crystals of submicron diameter, there is a change in the mechanism of growth, so quasicylindrical filamentous crystals of submicron diameter are formed by the mechanism of vapour-liquid-crystal (VLC), while the needle-like crystals of larger diameters are grown by the mechanism of vapour-crystal (VC) [18]. These different mechanisms lead to changes of the morphology and structure of

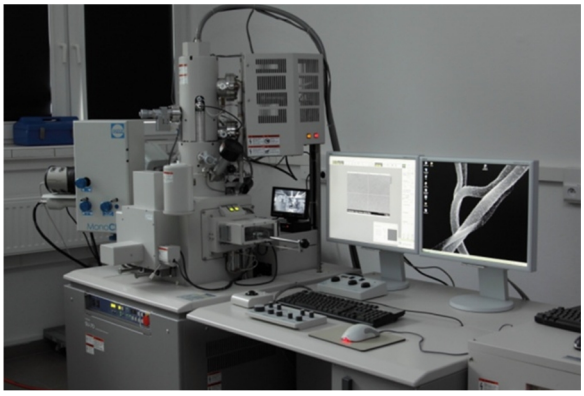

Fig. 1. Installation for structural research.

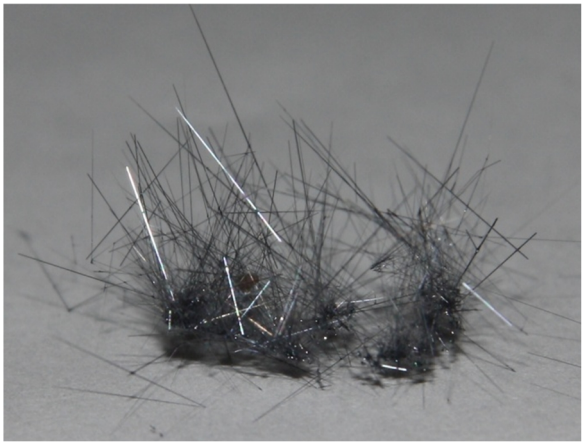

Fig. 2. Type of a bundle of $Si_{0,97}Ge_{0,03}$ whiskers.

crystals. Thus, submicronic whiskers are peculiar "heterostructures" that consist of a monocrystalline nucleus and a nanoporous shell [19]. Shaped whiskers (3 <d <80 microns) are single crystals with a well-defined facet [19].

Structural studies of SiGe whiskers were conducted at the Institute of Physics of the Polish Academy of Sciences (Warsaw) on a scanning electron microscope with a field emission (Schottky type) of the JEOL JSM-7600F company, built into the OXFORD X-ray spectrometer INCA 250. The general view of the equipment is shown in Fig. 1. Parameters of the microscope: accelerating voltage: 0,1 kV ÷ 30 kV; resolution of 1.0 nm (at 15 kV), 1.5 nm (at 1 kV); increase range: 25x ÷ 1000000x.

Experimental results have shown that the surface of crystals with diameters of 3-40 microns is mirrorless and has no significant defects (Fig. 2). According to the results of researches of these crystals by the method of Auger-spectroscopy with gradual anodic digestion of the surface, it was found that Br is located only on the surface of the whisker. Its surface concentration is $\approx 10^{14}$ cm^{-2}.

As the cross-sectional dimensions of the crystals increase, the surface becomes matte and there are growing steps.

In fig. 3 is a microphotography obtained on a scanning electron microscope, a surface of needle-like crystal with a transverse size of ≈ 60 μm, having a well-

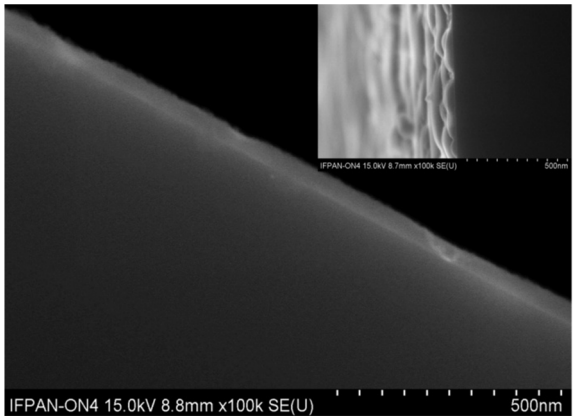

Fig. 3. SEM photo of whiskers thickness of ~ 60 μm.

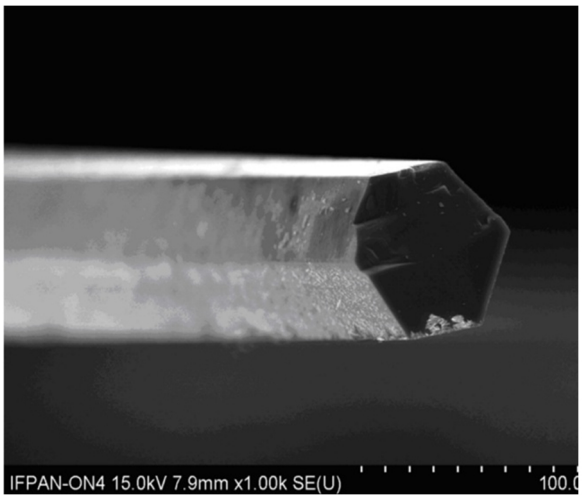

Fig. 4. The appearance of $Si_{0,97}Ge_{0,03}$ whiskers with a thickness of 60 μm.

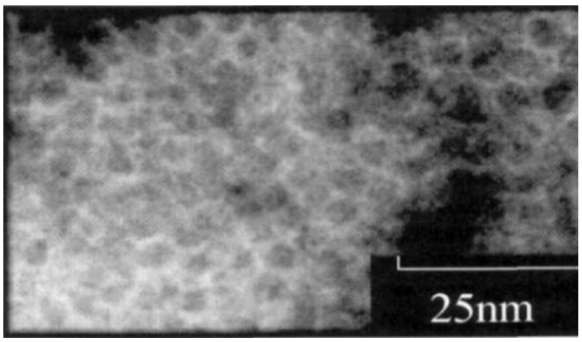

Fig. 5. Structure of porous shell of $Si_{0,97}Ge_{0,03}$ whiskers.

expressed hexagonal cut (see Fig. 4) [19]. The difference in the structure of the surface layer, thickness 50-60 nm, from the bulk part of the sample attracts attention. Its structure is similar to the crystalline structure of porous silicon (Fig. 5). As can be seen from Fig. 5 pores have dimensions of order 5-10 nm. Thus, as in the case of submicron whiskers, needle-like crystals with transverse dimensions greater than 50 microns contain nanoporous shell on the surface.

Fig. 6 and Fig. 7 presents the results of the study of impurity content in the crystal by scanning electron microscopy in the internal and superficial layers,

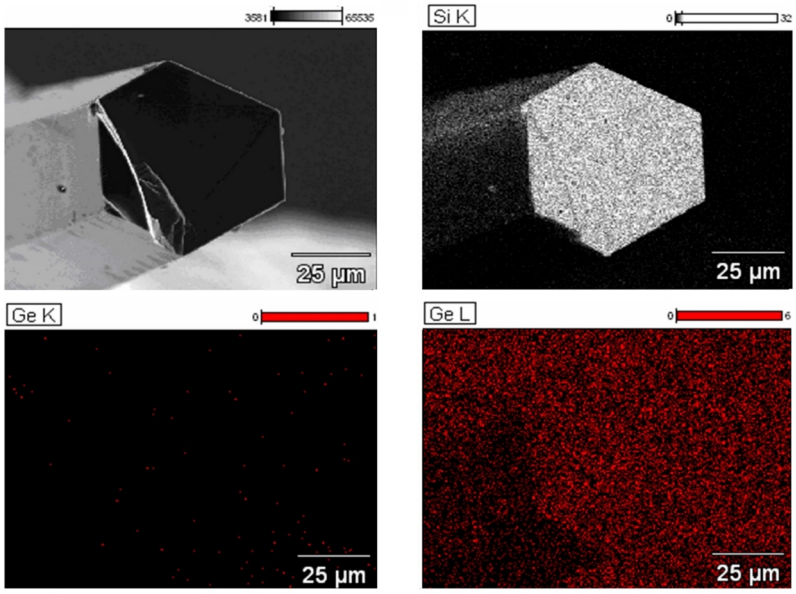

Fig. 6. Results of scanning electron microscopy of the inner layer of $Si_{0,97}Ge_{0,03}$ whiskers.

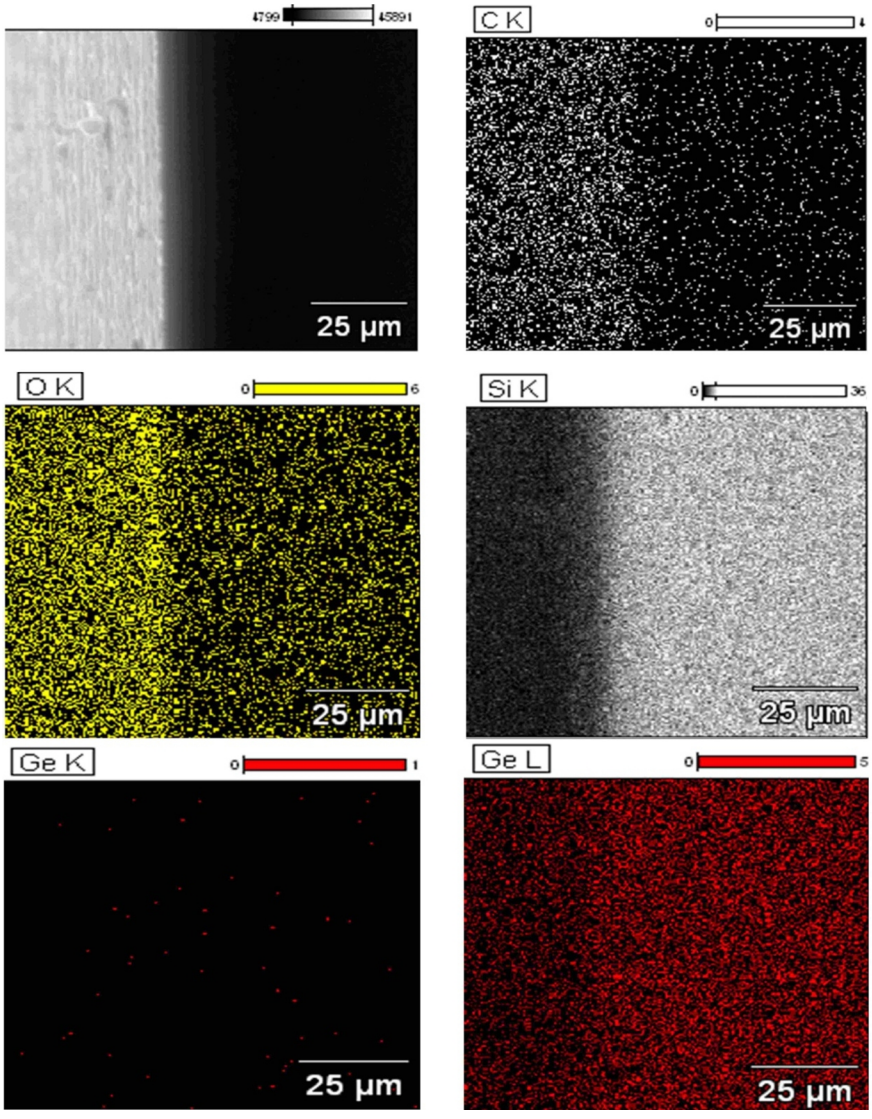

Fig. 7. Resulrs of scanning electron microscopy of the surface layer $Si_{0,97}Ge_{0,03}$ whiskers.

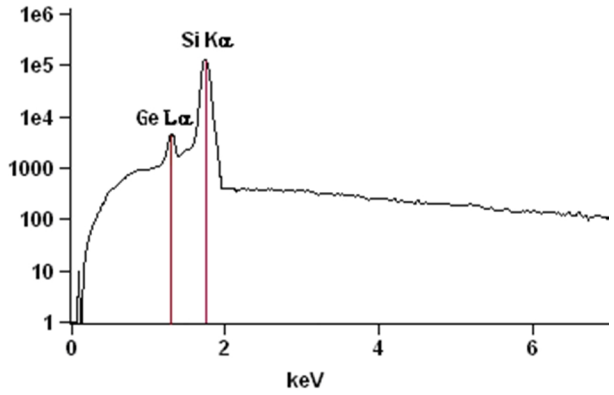

Fig. 8. Energy spectrum of X-ray radiation in the inner region of $Si_{0,97}Ge_{0,03}$ whiskers

Table 1

Elemental composition in the inner layers of $Si_{0,97}Ge_{0,03}$ whiskers

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
Si K	97.1	+/- 0.3	96.8	+/- 0.3
Ge L	2.9	+/- 0.1	3.2	+/- 0.1
Total	100.0		100.0	

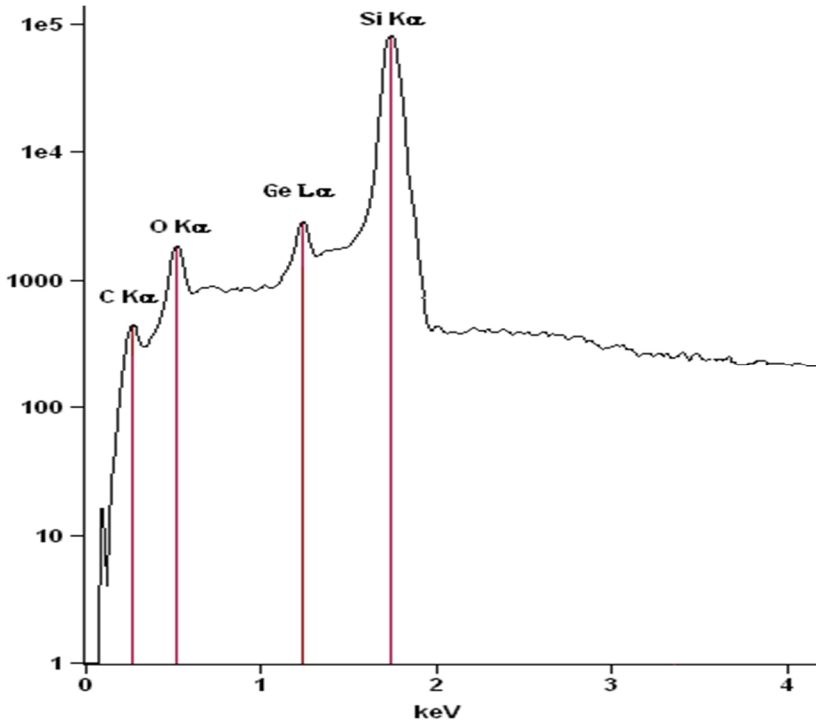

Fig. 9. Energy spectrum of X-ray radiation on the surface of $Si_{0,97}Ge_{0,03}$ whiskers

Table 2

Elemental composition on the surface of $Si_{0,97}Ge_{0,03}$ whiskers

Element Line	Weight %	Weight % Error	Atom %	Atom % Error
C K	1.5	+/- 0.1	2.2	+/- 0.1
O K	3.9	+/- 0.1	6.2	+/- 0.2
Si K	91.8	+/- 0.3	88.7	+/- 0.3
Si L	---	---	---	---
Ge L	2.8	+/- 0.3	2.9	+/- 0.1
Total	100.0		100.0	

respectively.

The results of the study of the X-ray radiation energy spectra and the determination of the elemental composition on the inner and outer layers are presented in Fig. 8, Table 1 and Fig. 9, Table 2, respectively. As is evident from the results obtained, the content of germanium is ~ 3%, which was assumed when calculating the loading of the growth chamber by appropriate elements.

From the energy spectrum obtained on the surface of $Si_{0,97}Ge_{0,03}$ whiskers with transverse dimensions of ~ 60 μm (Fig. 9) and from the results of the determination of the elemental composition (Table 2), it can be seen that the detected porous shell contains a significant concentration of oxygen and carbon atoms. It is obvious that the content of these components determines the peculiarities of the physical properties of filamentous crystals with transverse dimensions greater than 50 μm [17].

It should be noted that after etching 60 nm of the surface layer by the polishing procedure, the peaks of oxygen and carbon are not observed. Accordingly, one should expect to improve the physical properties of the samples.

We find this by examining the dependence of the magnetic susceptibility on the magnetic field intensity of these crystals.

Measurement of the magnetic coefficient was carried out by the Faraday method on a modernized equipment [20] in magnetic fields (0.3-5.0) kOe at room temperature T = 300 K. The accuracy of temperature stabilization reaches 1 K in the range of 70-300 K, and the accuracy of control of the magnetic field is about 1 Oe in the range of 0.2-5 kOe. When measuring the magnetic coefficient, the error in the field 4-5 kOe is ~ 0.7%, and in the field 0.2 kOe ~ 3%. The obtained experimental results are presented in Fig. 10.

As can be seen from the Figure 10, the presence of a surface layer with a significant concentration of oxygen and carbon atoms results in the appearance of a paramagnetic component of magnetic susceptibility and its nonlinear dependence on the magnetic field tension (Fig. 10, curve 1). Obviously, such results are due to the fact that the oxygen and carbon atoms are the main components of well-known paramagnetic complexes [21]. The presence of nonlinear dependence shows that a portion of paramagnetic centers forms magnetic nanoclusters that have superparamagnetic nature. Such clusters are described in the framework of the Langeven paramagnetism model of atoms. The difference is that the magnetic moments of such clusters are 10^3-10^5 times larger than the magnetic moments of individual atoms. Therefore, the general form of the formula describing this dependence is as follows [17]:

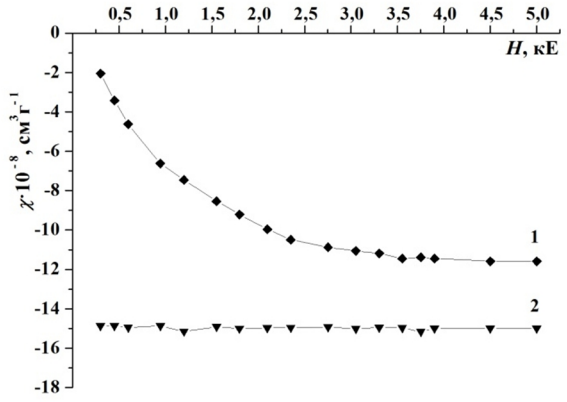

Fig. 10. Dependence of the magnetic susceptibility from magnetic field strength of $Si_{0,97}Ge_{0,03}$ whiskers with a thickness of ~ 60 μm: curve 1 – of grown whiskers; curve 2 – after etching of the surface layer.

$$c(H) = N_C N_0 M_B g\sqrt{s(s+1)} \cdot \left(\frac{N_0 M_B g\sqrt{s(s+1)}}{kT} \cdot \left(1 - \mathrm{cth}^2 \left(\frac{N_0 M_B g\sqrt{s(s+1)}}{kT} \cdot H \right) \right) + \right.$$

$$\left. + \frac{kT}{N_0 M_B g\sqrt{s(s+1)} \cdot H^2} \right) + + c_{par} + c_L ,$$

where N_K is the concentration of magneto-ordered clusters; N_0 is a number of paramagnetic centers in one magnetic cluster; $N_0 M_B g\sqrt{s(s+1)}$ – magnetic moment of the cluster; M_B – Bohr magneton; g is the g-factor; s – spin of the paramagnetic center, of which the cluster is composed (we accept s = 1/2); k – Boltzmann constant, T – temperature; c_{par} – paramagnetic component of susceptibility; c_L – the lattice susceptibility.

After the vaporization of the surface layer of the sample in the polishing agent, the nonlinearity disappears, and the magnetic susceptibility values coincide with the values of the magnetic susceptibility of structurally perfect samples $Si_{0,97}Ge_{0,03}$ (Fig. 10, curve 2) [22, 23].

Conclusions

The method of scanning electron microscopy and X-ray spectral microanalysis was conducted for structural investigations of filamentous $Si_{0.97}Ge_{0.03}$ crystals with a thickness of 60 μm. It is shown that these crystals have a clear hexagonal cut.

It was established that the microstructure of surface layers of filamentous crystals with transverse dimensions of 50-80 microns differs from bulk and

contains a significant concentration of oxygen and carbon atoms.

It has been established that the presence of a surface shell on crystals with transverse dimensions of 50-80 μm leads to a significant change in their magnetic properties.

It is shown that after etching a surface layer of 60 nm the thickness, the physical properties of the $Si_{0.97}Ge_{0.03}$ filament-shaped crystals are improved, which makes them promising for practical use.

Pavlovskyy Yu.V. - candidate of physical and mathematical sciences, associate professor, assistant professor of technological and professional education department;
Grzegorz Łuka - Ph.D., Senior Researcher, Physics Department;
Ostrovskyy I.P. - doctor of technical sciences, professor, professor of the department of semiconductor electronics;
Pavlovska N.T. - candidate of physical and mathematical sciences, teacher of physics.

[1] S.V. Sazhnev, M.A. Fomichev, V.N. Timofeyev. Nano- i mikrosistemnaya tekhnika. (1), 39, (2008).
[2] F. Zhang, Y. Ding, Y. Zhang, X. Zhang, Z. Wang. ACS Nano. 6(10), 9229, (2012).
[3] X.T. Zhou, J.Q. Hu, C.P. Li, D.D. Ma, C.S. Lee, S.T. Lee. Chemical Physics Letters. 369, 220 (2003).
[4] I. Maryamova, A. Druzhinin. E. Lavitska, I. Gortynska, Y. Yatzuk. Sensors and Actuators. A85(1-3), 153, (2000).
[5] A.A. Druzhinin, I.P. Ostrovskiy, S.M. Matviyenko, YU.R. Kogut. Tekhnologiya i konstruirovaniye v elektronnoy apparature. (1), 26, (2005).
[6] R. Baitsar, V. Voronin, E. Krasnogenov, N. Bogdanova. Sensors and Actuators. A30, 175, (1992).
[7] V. Voronin, I. Maryamova, Y. Zaganyach, E. Karetnikova, A. Kutrakov. Sensors and Actuators. A30, 27, (1992).
[8] A.A. Druzhinin, I.I. Maryamova, Ye.N. Lavitskaya, A.P. Kutrakov. Datchiki i sistemy. (6), 2, (2001).
[9] A.O. Druzhynin, I.Y. Maryamova, O.P. Kutrakov, N.S. Lyakh-Kahuy. Fizyka i khimiya tverdoho tila. 12(4), 1078, (2011).
[10] Ya. Yang, Yu. Zhou, J.M. Wu. ACS Nano. 6(9), 8456, (2012).
[11] A. Druzhinin, I. Ostrovskii, N. Liakh-Kaguy. Journal of Thermoelectricity. (4), 82, (2009).
[12] V. Krivitsky, L. Hsiung, A. Lichtenstein, B. Brudnik, R. Kantaev, R. Elnathan, A. Pevzner, A. Khatchtourints, F. Patolsky. Nano Lett.12(9), 4748, (2012).
[13] F. Patolsky, G. Zheng C. M. Lieber. Nanomedicine. 1(1), 51, (2006).
[14] Y. Zhou, Y. Liu, J. Cheng Y. Lo. Nano Lett. 12(11), 5929, (2012).
[15] V.A. Voronin, I.L. Maryamova, A.S. Ostrovskaya. Cryst. Prop. and Prepar. 36-39, 340, (1991).
[16] P.H. Lytovchenko, N.T. Pavlovska, YU.V. Pavlovskyy, I.P. Ostrovskyy. Aktualni problemy fizyky, matematyky ta informatyky. Shchorichnyy naukovyy zhurnal. (6), 2, (2014).
[17] V.M. Tsmots, P.G. Litovchenko, N.T. Pavlovska, Yu.V. Pavlovskyy, I.P. Ostrovskyy. Semiconductors. 44(5), 623, (2010).
[18] E.I. Givargizov. Rost nitevidnykh i plastinchatykh kristallov iz para (Nauka, Moskva, 1977).
[19] A.I. Klimovskaya, I.V. Prokopenko, I.P. Ostrovskii. J. Phys. Condens. Matter. 13, 5923, (2001).
[20] Pat. 77284 Ukraina, MPKG01R 33/16. Prystriy dlya vymiryuvannya mahnitnoi spryynyatlyvosti materialiv / V.M. Tsmots, I.S. Pankiv, L.I. Pankiv, YU.V. Pavlovskyy, V.V. Petrenko, T.S. Kavetskyy, D.V. Labovka, M.M. Luchkevych, R.V. Okhrymovych, V.P. Salan, M.V. Tsyuper. – 20041008650; zayavl. 25.10.2004; opubl. 15.11.2006, Byul. №11.
[21] G.P. Gaydar. Elektronnaya obrabotka materialov. 48(1), 93, (2012).
[22] V. Zmots, P. Litovchenko, Yu. Pavlovskyy, I. Ostrovskyy, O. Litovchenko, M. Luchkevich, I. Pankiv, V. Salan. Ukrainian Journal of Physical. 53(1), 36, (2008).
[23] A. Druzhinin, I. Ostrovskii, Yu. Khoverko, P. Litovchenko, N. Pavlovska, Yu. Pavlovskyy, Yu. Ugrin. Journal of Magnetism and Magnetic Materials. 393(1), 310, (2015).

Ю.В. Павловський[1], Г. Лука[2], І.П. Островський[3], Н.Т. Павловська[4]

Структура та магнітні властивості голкоподібних кристалів $Si_{0,97}Ge_{0,03}$

[1]Дрогобицький державний педагогічний університет імені Івана Франка, вул. І. Франка, 24, 82100, Дрогобич, Україна, yu_pavlovskyy@ukr.net
[2]Інститут фізики польської академії наук, 02-668 Варшава, Польща
[3]НУ «Львівська політехніка», вул. С. Бандури, 12, 79013, Львів, Україна
[4]Дрогобицька загальноосвітня школа І-ІІІ ступенів №4, вул. Стрийська, 28, 82100, Дрогобич, Україна

Методом хімічних транспортних реакцій у закритій галоїдній системі Si-Au-Pt-B-Br вирощено ниткоподібні кристали $Si_{1-x}Ge_x$ складу x = 0,01 - 0,08 поперечними розмірами 0,1 - 100 мкм. Досліджено структурні та магнітні властивості одержаних кристалів. Методом скануючої електронної мікроскопії показано, що на поверхні голкоподібних кристалів, поперечними розмірами 50 – 80 мкм, присутня пориста оболонка товщиною 50 – 60 нм. З аналізу енергетичний спектрів рентгенівського випромінювання встановлено, що поверхнева оболонка містить значну концентрацією атомів кисню та вуглецю. У свою чергу, на внутрішніх шарах зразків піків кисню та вуглецю не виявлено. Встановлено, що стравлювання поверхневого шару кристалів приводить до покращення їх структурних та магнітних властивостей.

Ключові слова: кремній-германій, голкоподібні кристали, електронна мікроскопія, рентгенівський спектр, магнітна сприйнятливість.