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Synthesis of Porous Germanium with Silver Nanoparticles by Ion Implantation

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Abstract—The synthesis of porous PGe layers with Ag nanoparticles is considered when implanted with Ag^+ ions of single-crystal *c*-Ge with an energy of 30 keV at a dose of 1.5×10^{17} ion/cm^2 and a current density in the ion beam of 5 μA/cm^2. Scanning electron and atomic force microscopy, as well as X-ray microprobe analysis and the diffraction of reflected electrons, have shown that, as a result of implantation, a porous amorphous PGe layer of a spongy structure consisting of a grid of intersecting nanofilaments with an average diameter of ~10–20 nm is formed on the *c*-Ge surface. At the ends of the filaments, the formation of Ag nanoparticles is observed. It is found that the formation of pores during implantation with Ag^+ ions is accompanied by the effective spraying of the Ge surface.

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INTRODUCTION

Apparently, the history of the study of porous germanium (PGe) begins with the work [1], in which the sputtered thin Ge films with local voids (pores) in their structure were studied. Later, various technological approaches were used to obtain PGe. The first direct evidence of the formation of the PGe structure by ion implantation on the surface of a single-crystal *c*-Ge was obtained by electron microscopic observations, *c*-Ge irradiation being performed with 50 keV Ge^+ ions [2]. Subsequently, the porous structure was recorded, as is shown in the review [3], for amorphous (*a*-Ge) and *c*-Ge substrates at low-energy and high-energy (>1 MeV) implantation with various ions such as Ga^+, Ge^+, Mn^+, Ni^+, In^+, Sn^+, Sb^+, I^+, Au^+, and Bi^+. Separately, let us note the works [4–7], in which implantation with Ag^+ ions at high energies of 100 MeV (but rather small doses in the range 5.0×10^{12}–2.0×10^{14} ion/cm^2) was used to create PGe layers and their crystallization. The present work is also devoted to the creation of PGe layers by ion implantation, but the goal is to synthesize Ag nanoparticles in a PGe structure (Ag:PGi) simultaneously with the formation of the structure. For this purpose, it is proposed to use the low-energy (<100 keV) high-dose (>1.0×10^{17} ion/cm^2) implantation of *c*-Ge with Ag^+ ions for the first time, much as similar conditions of irradiation successfully yielded the synthesis of porous Si layers with Ag nanoparticles [8–11]. The interest in porous semiconductor structures with nanoparticles of noble metals exhibiting plasmon-resonance properties is due to the prospects of their use in various applications: to increase absorptivity in solar cells [12], improve photoconductivity [13], generate electron–hole pairs [14], etc.

EXPERIMENTAL

The formation of a PGe layer with metallic nanoparticles was carried out on a 0.5-mm GES-40 *c*-Ge polished substrate. To do this, implantation with 30 keV Ag^+ ions was performed at an irradiation dose of 1.5×10^{17} ion/cm^2 and a current density in the ion beam of 5 μA/cm^2 on an ILU-3 ion accelerator. The morphology of the structured surface of the implanted *c*-Ge was studied on an (SEM) SU 8000 (Hitachi) scanning electron microscope and a Merlin (Carl Zeiss) scanning electron microscope equipped with an HKL NordLys (Oxford Instruments) diffractive optical element (DOE) detector. The elemental composition in the sample was monitored by energy-dispersive X-ray microanalysis using an Aztec X-Max SEM spectrometer (Oxford Instruments).

To determine the appearance of the step due to sputtering or swelling of the surface at the boundary of the irradiated and unirradiated parts of the sample, a mesh nickel mask with square 20 μm cells was superimposed on the *c*-Ge substrate portion during irradiation. The step profile was measured on a FastScan (Bruker) atomic force microscope (AFM).

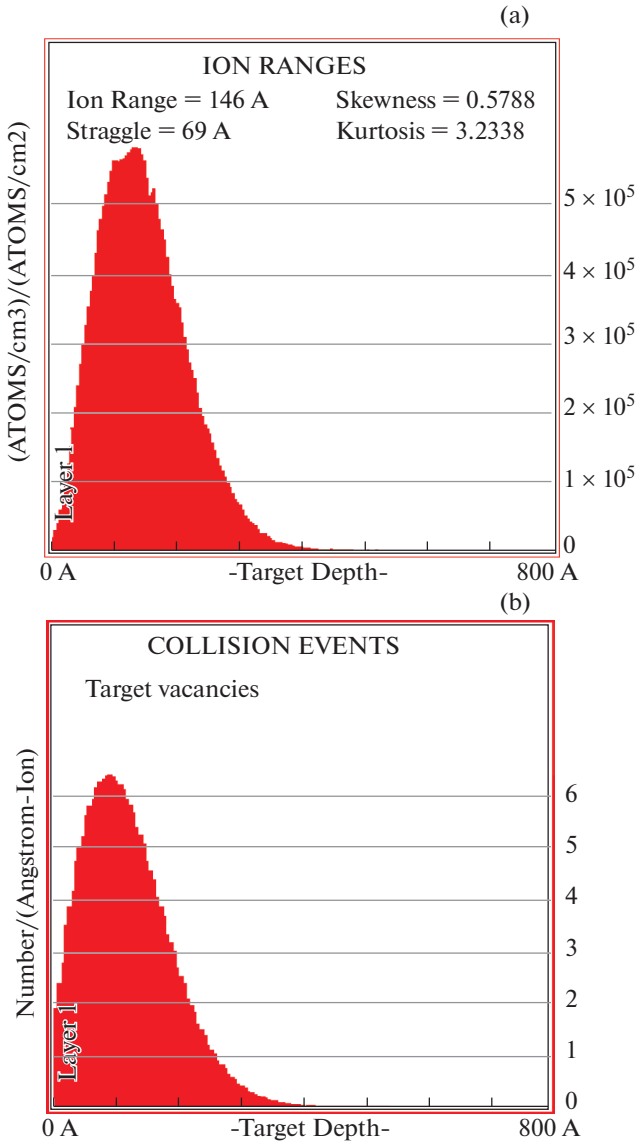

Fig. 1. Simulated profiles of the distribution of (a) implanted Ag^+ ions and (b) generated vacancies in Ge irradiated with an energy of 30 keV.

RESULTS AND DISCUSSION

Using the SRIM-2013 computer program (www.srim.org) and its procedure for modeling profiles of the distribution of implanted ions and generated vacancies by depth in irradiated matrices [17], in the present work the corresponding dependences of the distribution of Ag^+ ions in Ge at their energy acceleration of 30 keV (Figs. 1a, 1b) have been calculated. It follows from these dependences that, in the initial period of irradiation, in the near-surface region of Ge there is an accumulation of silver atoms with a maximum of the statistical distribution of concentration over the Gaussian curve at a depth of $R_p \sim 14.6$ nm, and the scatter of the ion range from R_p is $\Delta R_p \sim 6.9$ nm

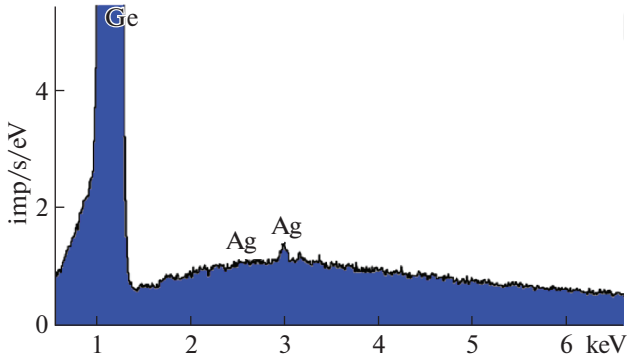

Fig. 2. Spectra of energy-dispersive X-ray microanalysis of Ge implanted with Ag^+ ions.

(Fig. 1a), the thickness of the implanted layer being estimated as $R_p + \Delta R_p = 28.4$ nm. However, as will be shown below, prolonged irradiation, simultaneously with the formation of PGe and the segregation of silver at the surface, results in an effective sputtering of Ge. The profile of the generated vacancies in Ge when implanted with Ag^+ ions has the same form and practically coincides with the distribution of Ag^+ ions over the depth of the sample (Fig. 1b).

An energy dispersive X-ray microanalysis of the implanted Ge surface is characterized by a spectrum with two Ag peaks in the energy range 2.5–3.5 keV (Fig. 2), which were not observed in the spectrum of unirradiated Ge.

SEM images of the surface of Ge implanted with Ag^+ ions at various scales are shown in Fig. 3. As one can see from the figure, after carrying out ion implantation, the polished surface of the *c*-Ge substrate undergoes a significant change; its morphology appears to be a highly developed open porous spongy structure of PGe. Let us note that such a spongy structure of PGe is formed when Ge is implanted with, e.g., a Bi^+ ion with an energy of 30 keV [5], but differs significantly from the columnar type PGe formed by implantation with a lighter Ge^+ ion [3, 16]. In general, the possibility of creating pores by implantation with Ge^+ ions indicates that the formation of pores is due not to the presence of an impurity, but to the specific energy conditions of irradiation [5], which may also be assumed for our case, Ag : PGi, although a heavy impurity may stimulate the appearance of a spongy structure. The morphological homogeneity of the Ag : PGe surface observed on a sufficiently large sample area of tens of microns (Fig. 3a) indicates that the porous structure is not a random local artifact of surface change during implantation and may be characterized by the concept of scalability important for certain technological applications. An increase in the scale of the surface fragment (Figs. 3b, 3c) more clearly shows the spongy structure of the pores, consisting of intertwining Ge nanofilaments (dark gray)

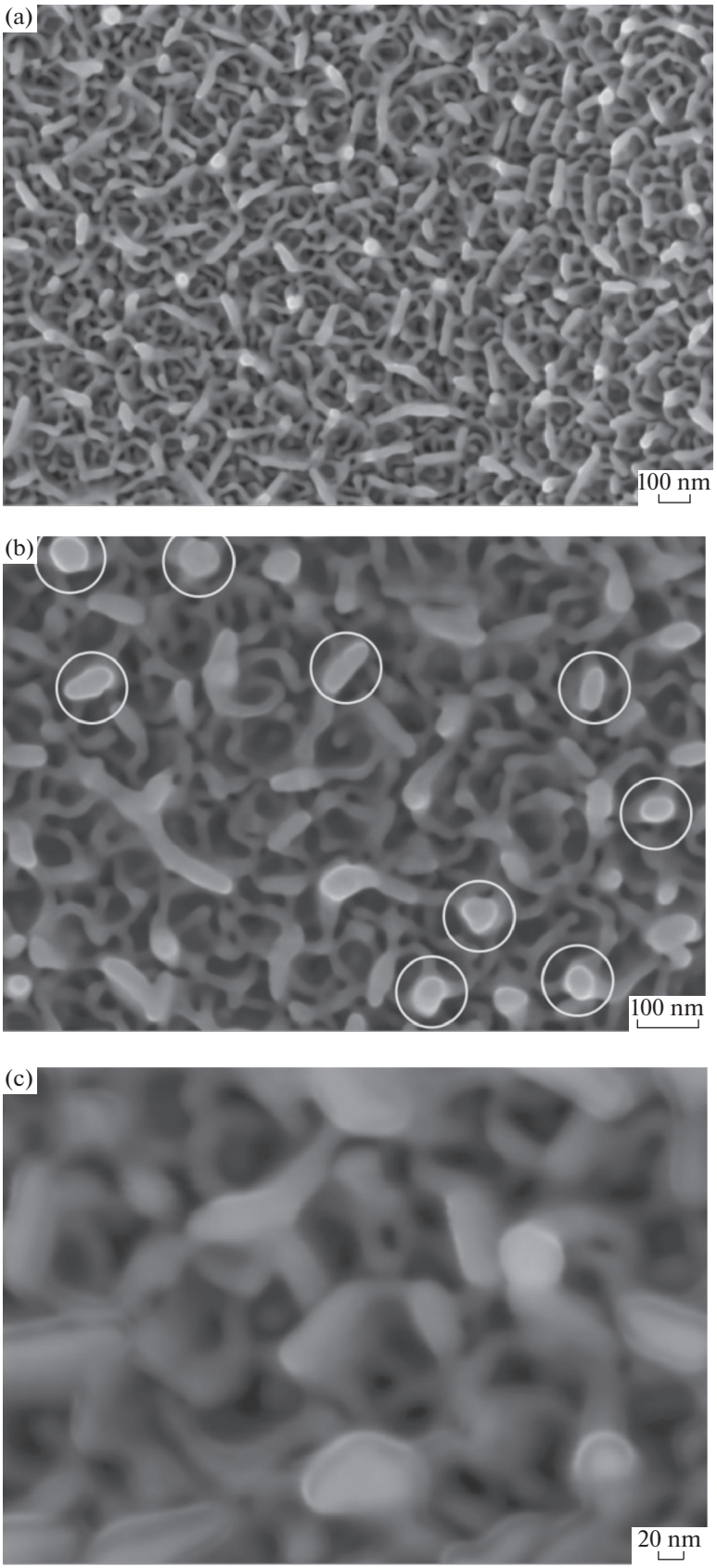

Fig. 3. SEM images of the PGe surface formed by the low-energy high-dose implantation of Ag^+ ions in *c*-Ge shown at various scales.

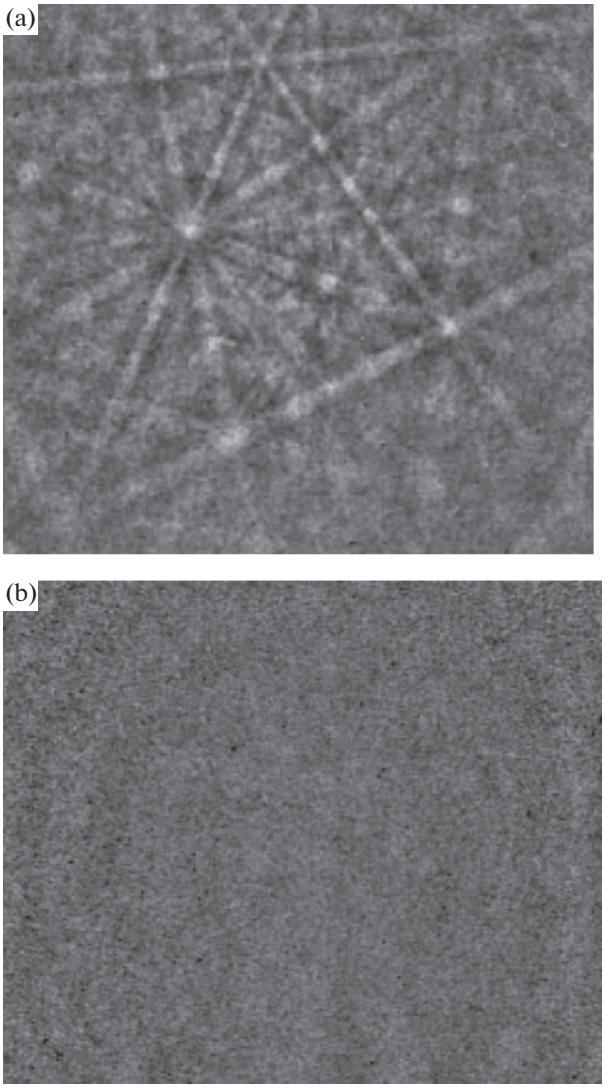

Fig. 4. (a) DOE images from (a) the surfaces of the initial *c*-Ge substrate and (b) the same substrate implanted with Ag^+ ions.

with an average diameter on the order of 10–20 nm. At the ends of Ge nanofilaments, 20–30 nm ion-synthesized nanoformations (light spots) close to spherical are observed. For clarity, some of these nanoformations are outlined in Fig. 3b by circles. Since the heavier chemical elements detected by the backscattered electron detector appear on SEM images in a lighter tone, for a composite material consisting only of Ge atoms and implanted Ag, one can assume that bright areas recorded on a slightly dark background (signal from Ge)—nanoformations—are determined by the metallic Ag in the form of nanoparticles. It should be noted that the solubility of Ag in Ge is exceptionally small ($\sim 10^{16}$ at/cm^{-3}), and, for the dose of 1.5×10^{17} ion/cm^2, analogous to various implanted semiconductors and dielectrics [11], the generation of metallic Ag in Ge is quite realistic. It should also be noted that Ag atoms do not form any chemical compounds with Ge. A similar situation was observed earlier on SEM images for porous layers of PSi and PGeSi with Ag nanoparticles formed by the implantation of Ag^+ ions [8, 10, 18]. At maximum magnification (Fig. 3c), one can see that the thickness of the Ge filaments is somewhat inferior to the sizes of Ag nanoparticles.

The structural characterization of the surface of the initial and implanted Ge was carried out when registering the DOE images (Fig. 4). Figure 4 shows an experimentally observed Kikuchi diffraction pattern in the reflected electrons of the unirradiated *c*-Ge (Fig. 4a), from which it follows that the *c*-Ge substrates used in the work are characterized by a single-crystal cubic structure with the parameters $a = b = c =$ 5.66 Å and $\alpha = \beta = \gamma = 90°$. For the surface of an implanted Ag : PGe sample, in contrast to the Kikuchi diffraction, in the form of bands parallel to the planes of the crystal lattice, a DOE pattern consisting of the wide diffuse rings (Fig. 1) is observed, reflecting lattice destruction and the formation of an amorphous PGe layer.

As is customary in the practice of ion implantation, in particular, in the case of Ge [5, 15, 16], implantation through a mask is used to control the processes of sputtering or swelling of the surface of the irradiated material. The SEM image of the Ge surface containing the fragments of PGe microstructures formed in this work by implantation with Ag^+ ions through a mask is shown in Fig. 5. For an independent evaluation of the topology of the surface after implantation, observations were made at various scales and on two different SEM-SU 8000 (Fig. 5a) and Merlin (Fig. 5b) microscopes. As one can see from the images, as a result of implantation on the Ge surface, square deepened sections of PGe are formed bounded by the walls of unirradiated *c*-Ge, which indicates the spraying of the Ge surface rather than its swelling. According to the AFM data, the depth of sputtering of the sections, which is ~200 nm, was estimated. The SEM image at a larger magnification at the corner of the square cell (Fig. 5c) clearly demonstrates the formation of spongy PGe on the implanted region of the cell. From the mass ratios of Ge and Ag atoms, as well as the relatively low implantation energy, one can speak of the dominance of nuclear collisions of accelerated Ag^+ ions with the substrate atoms and, as a result, the latter are spattered by the mechanism of directly knocking them out of the target [19]. This result seems to be important from the point of view of determining the pathways for the formation of PGe, and it turns out to be somewhat unexpected, as it was previously shown that the formation of pores in Ge implanted with Ge^+ ions was accompanied by the opposite phenomenon—surface swelling [16]. Therefore, the mechanism of pore formation in implanted Ge, based on the generation and

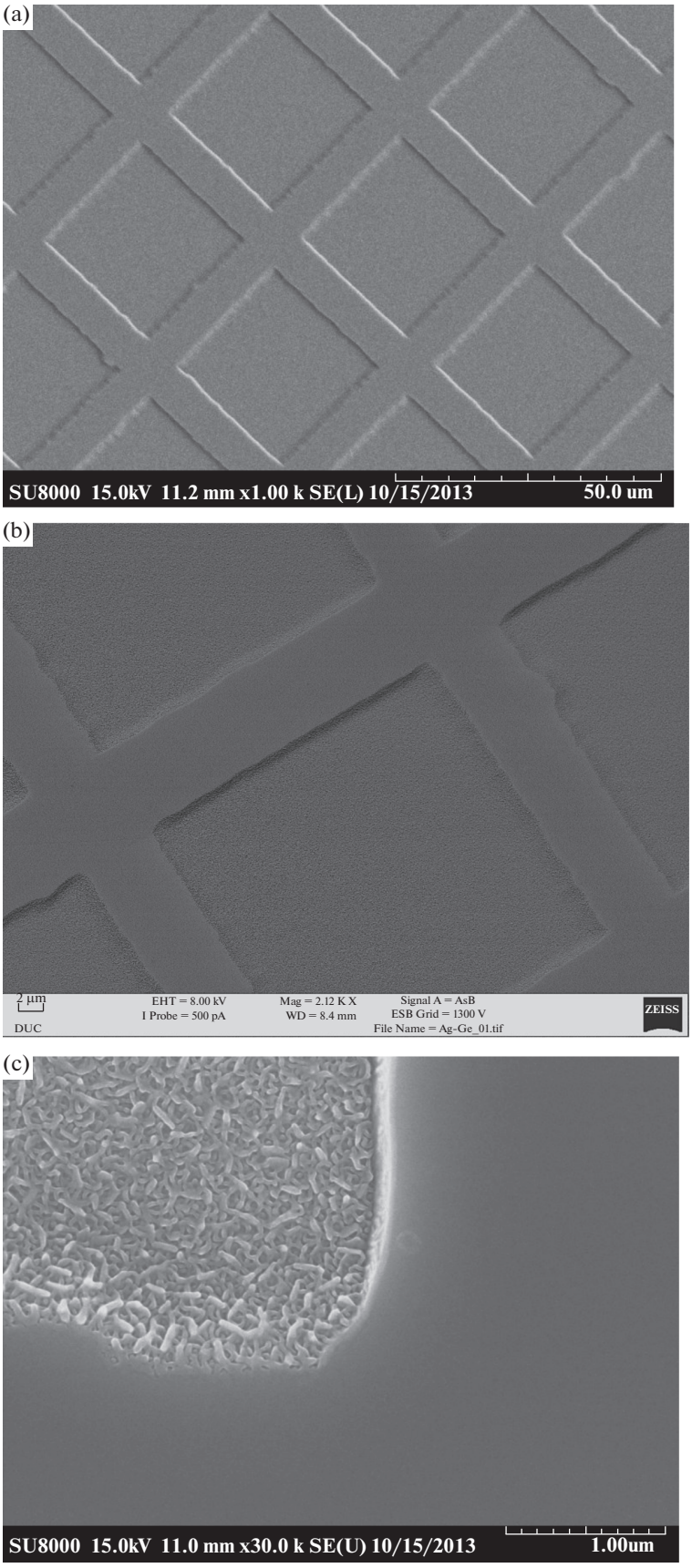

Fig. 5. SEM images, shown at different scales, of periodic microstructures on the *c*-Ge surface with PGe regions obtained by implantation with Ag^+ ions through a mask.

unification of vacancies in an irradiated semiconductor, proposed, e.g., in [16], cannot be simply transferred to the case of *c*-Ge implantation with Ag^+ ions. Separately, the paper [20] should be mentioned, in which it is postulated that, when implanting the *c*-Ge substrate with ions of groups 1–7 of the periodic table with masses of $M_i > 72$ (Ag^+, Cd^+, In^+, As^+, Sb^+, Te^+, and I^+) at energies of 30–180 keV, the characteristics of the implanted layers common to all ions should appear above the critical dose. First, a loosened area called the ultradispersed medium, which swells and forms a step above the unirradiated part of the substrate, appears and, second, it is said that the implanted layer is a polycrystalline Ge structure with small crystallites. As proof of the generality statement for all ions, experimental results are given (by etching and subsequent sample weighing, as well as by recording electron diffraction patterns) for only one type of Sb^{2+} at a dose of 1.8×10^{16} ion/cm^2 and an energy of 80 keV. However, as follows from the data presented in this paper, for the case of implanting *c*-Ge with Ag^+ ions, the opposite picture is observed: the atomization of the Ge surface and formation of an amorphous layer from the PGe spongy structure.

CONCLUSIONS

Thus, in the present work we have observed the formation of PGe layers with Ag nanoparticles on the *c*-Ge surface during low-energy high-dose implantation. It is found that the implantation results in the ion sputtering of the surface, on which a spongy amorphous porous structure is formed. Ion implantation is used in industrial semiconductor microelectronics to form various types of Ge and GeSi nano- and microdevices. Therefore, the considered method of obtaining PGe by irradiation with Ag^+ ions may be integrated quite easily in modern industrial process of improving the technology of manufacturing microcircuits.

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