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Formation of nanoporous germanium layers on thin films obtained by ion-assisted deposition

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The present study is aimed to test a possibility for formation of nanoporous *a*-Ge layers by implantation with Ag^+ ions thin amorphous film a-Ge obtained by the original method of ion-assisted deposition. For this purpose, *c*-Ge target was sputtered with low-energy Xe^+ ions onto a quartz glass substrate coated with a conductive Ni layer. Ion implantation was performed at an energy of $E = 30$ keV, a current density of $J = 5\,\mu$A/cm^2 and doses of $D = 2.0 \cdot 10^{16}$ and $6.0 \cdot 10^{16}$ ion/cm^2. Electron microscopy and optical reflectance spectroscopy were used to analyze the formed material. It was shown that at a low implantation dose the film surface remains smooth, whereas an increase in the dose leads to the formation of a nanoporous Ge layer consisting of needle-like structures randomly located in the plane of the sample surface.

Keywords: nanoporous germanium, ion-assisted deposition, ion implantation.

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The advancement of lithium-ion battery technology by searching new composite materials for anodes is one of the priority areas of both fundamental and applied research. As was demonstrated in the work [1], IV group elements, such as Si, Ge, Sn, etc., could be used to fabricated anodes with high capacitive characteristics. Of these, since high electronic conductivity, Ge is the most promising, which is coupled with a sufficient capacity, increases significantly the charge/discharge rate of batteries [2]. Nanoporous germanium (PGe), which is characterized by a large specific area, has certain advantages in this context, since the mentioned feature raises the efficiency of chemical reactions in electrolytes [3]. In addition, PGe layers are promising photonic and optoelectronic nanomaterials that may be used efficiently in thermoelectric photoconverters and solar cell elements [4], infrared absorption gas sensors [5], as biosensors [6], as scaffold structures for growing ultra-small bacteria or biofilms in clinical and biomedical research [7], for fabrication of chemical sensors based on the SERS effect [8], etc.

One commonly used approach for the formation of thin PGe layers is ion implantation of Ge substrates [9]. Various types of Ge substrates have been used in practice to obtain PGe: single-crystal *c*-Ge wafers [9], epitaxial Ge layers [10], and *a*-Ge films produced by magnetron deposition [11]. The search for new methods to reduce further the cost of the PGe formation process is ongoing, since the production of crystalline semiconductor substrates is cost-intensive. The aim of the present study is to examine the possibility for production of PGe by low-energy high-dose implantation with Ag^+ ions into a thin *a*-Ge film of (TFGe) synthesized by a relatively inexpensive original ion-assisted deposition technique. This approach was proposed and tested successfully in fabrication of thin dielectric films [12]. The idea behind the proposed technology is the deposition of a chosen material from a target, which is irradiated and simultaneously sputtered by low-energy ions of an inert gas, onto a substrate. Moreover, this technology allows one to deposit a conductive metal layer for technical purposes prior to the synthesis of TFGe in the same vacuum chamber, which is hard to achieve when *c*-Ge substrates are used.

An original vacuum setup for ion-assisted deposition of chemically homogeneous thin films was used to deposit TFGe. A *c*-Ge target was sputtered by Xe^+ ions onto a quartz glass substrate coated with a conductive Ni layer with thickness $L_{Ni} = 200$ nm in vacuum ($\sim 2 \cdot 10^{-2}$ Pa). A Kaufman ion source used in this setup was operated in the following regime: energy of Xe^+ $E = 1$ keV and current density $J = 100\,\mu$A/cm^2. A film of amorphous *a*-Ge with thickness $L_{TFGe} = 150$ nm was deposited during ~ 10 min. The method for deposition of a Ni layer by sputtering a bulk target with Xe^+ ions at $E = 1$ keV was detailed in the work [13]. The root-mean-square surface roughness was determined with a Dimension FastScan (Bruker) scanning probe microscope and did not exceed $\sigma = 1$ nm for the deposited Ni layer and TFGe.

The parameters of Ag^+ ion implantation were as follows: $E = 30$ keV, $J = 5\,\mu$A/cm^2, $D = 2.0 \cdot 10^{16}$ and $6.0 \cdot 10^{16}$ ion/cm^2. An ILU-3 ion accelerator was used. The irradiated target was kept at room temperature. The sample surface morphology was examined with a Merlin (Carl Zeiss) scanning electron microscope (SEM) at an accelerating voltage of 5 kV and a current density of 300 pA. Optical reflection spectra of samples in the range of 350–1100 nm were measured with an AvaSpec-2048 (Avantes) waveguide spectrometer.

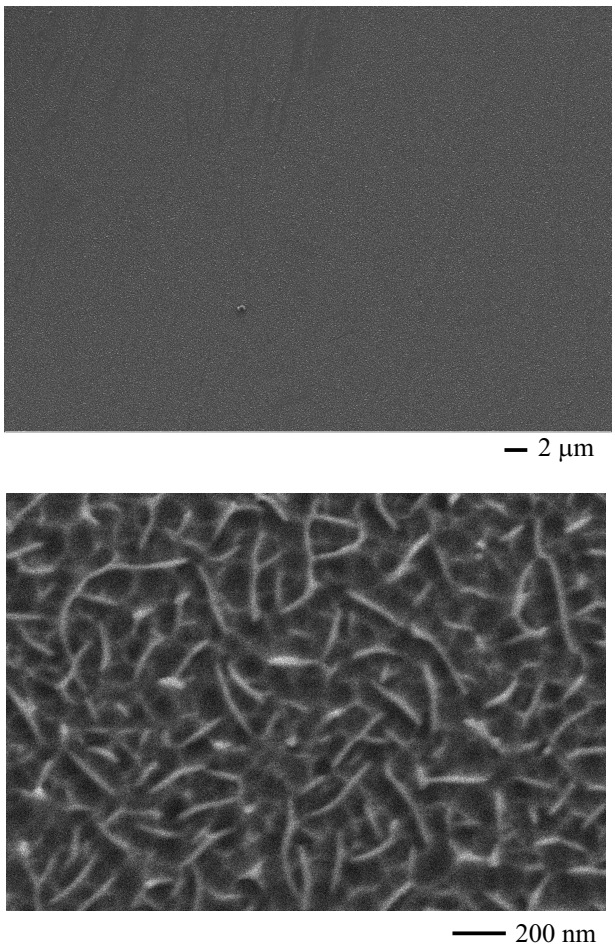

Figure 1. SEM image of the TFGe surface implanted with Ag^+ ions at $E = 30$ keV, $J = 5\,\mu$A/cm^2, and $D = 2.0 \cdot 10^{16}$ (*a*) and $6.0 \cdot 10^{16}$ (*b*) ion/cm^2.

The DYNA computer code was used to evaluate the profiles of nonuniform depth distribution of implanted Ag^+ ions with $E = 30$ keV within the Ge sample. The physical principles of calculation utilized in DYNA were discussed in detail in the work [14]. This code relies on the approximation of binary collisions between accelerated ions and atoms of the irradiated matrix. These collisions induce a dynamic (dependent on irradiation time) change in the elemental composition of the implanted substrate layer, the concurrent variation of which due to surface sputtering is also taken into account. The obtained results suggest that implanted Ag^+ ions in Ge follow a Gaussian statistical curve of dopant distribution with its maximum at depth $R_p \sim 14.6$ nm and straggle $\Delta R_p \sim 6.8$ nm. The thickness of the near-surface doped layer (with surface sputtering during implantation taken into account) was estimated as $h = R_p + 2\Delta R_p$ at approximately 30 nm. This h value is significantly lower than L_{TFGe}.

Figure 1*a* shows the SEM image of the TFGe sample surface after implantation with $D = 2.0 \cdot 10^{16}$ ion/cm^2. It is evident that the sample surface appears smooth and, similar to the surface of non-implanted TFGe, lacks any significant morphological features. Irradiation with Ag^+ ions at higher values of $D = 6.0 \cdot 10^{16}$ ion/cm^2 leads to the creation of a PGe structure on amorphous TFGe in the form of nanostructured needle-like formations of approximately the same size that are oriented randomly in the surface plane (Fig. 1*b*). It should be noted that a similar PGe nanostructure was observed for the first time on *c*-Ge substrates implanted with Ag^+ ions at significantly lower energies $E = 10$ keV while at $E = 30$ keV, PGe of a different morphology (a spongy structure of intertwined Ge nanowires) was formed on [15]. The exact mechanisms governing the formation of PGe layers of different morphology was not determined yet, although it was discussed in detail in literature [9–11,15].

The optical reflectance spectra of the virgin TFGe structure, implanted samples, and (for comparison) the *c*-Ge substrate are shown in Fig. 2. The *c*-Ge spectrum is characterized by bands with maxima at 276, 564, and 820 nm (curve *1*), which are shaped by intraband and interband electron transitions [16]. The degree of crystallinity of Ge is determined by the intensity of the reflection band with a maximum at 276 nm [17]. As seen the TFGe reflectance spectrum lacks short-wavelength reflection bands at 276 and 564 nm, characterizing the structure of the deposited film as an amorphous one (curve *2*). At the same time, the presence of local nanosized regions of a quasi-crystalline ordered structure in the deposited layer cannot be excluded.

Reflection coefficient R of TFGe substrates implanted with Ag^+ ions decreases consistently with an increase with D, especially in the short-wavelength region of the spectra (curves *3* and *4*). This suppression of reflectance is attributable to additional disordering of the implanted TFGe layer at the nanolevel (increase in concentration of vacancies and interstitial defects) and the microlevel (emergence of porosity). An integral suppression of

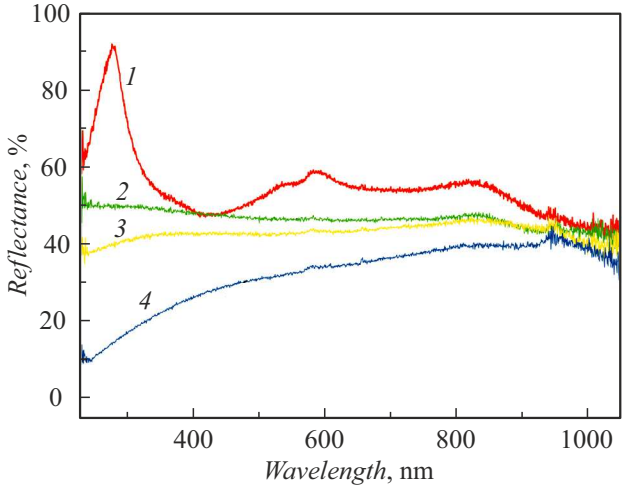

Figure 2. Optical reflectance spectra of the *c*-Ge substrate (*1*), the virgin TFGe (*2*), and TFGe implanted with Ag^+ ions at $D = 2.0 \cdot 10^{16}$ (*3*) and $6.0 \cdot 10^{16}$ (*4*) ion/cm^2.

reflectance after amorphization of the surface layer of *c*-Ge implanted with $^{59}Ni^{+}$ ions was observed in the work [18], although the Ge surface morphology was found to remain unchanged. Therefore, one should note an additional cause of reduction in reflectance of implanted TFGe: intense Rayleigh scattering by surface nanostructures [19,20].

Thus, the possibility for formation an amorphous TFGe structure by ion-assisted deposition in the process of sputtering of a *c*-Ge target by low-energy Xe^{+} ions onto a substrate of quartz glass coated with a conductive Ni layer was demonstrated. The technique of high-dose implantation of TFGe by Ag^{+} ions with $E = 30\,\text{keV}$, $J = 5\,\mu\text{A/cm}^2$, and $D = 6.0 \cdot 10^6\,\text{ion/cm}^2$ allows one to form a thin-film amorphous PGe layer with a needle-type morphology and a chaotic distribution of needles in the surface plane. It may also be concluded that the specific type of morphological PGe structures is set not only by the parameters of ion implantation, but also by the features of fabrication of the Ge matrix for its irradiation.

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Conflict of interest

The authors declare that they have no conflict of interest.

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