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Formation of a diffraction grating based on nanoporous germanium by implanting bismuth ions

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A diffraction grating was formed on the basis of a nanoporous Ge (PGe) layer by irradiating a single-crystal c-Ge (Bi:PGe) substrate with the $^{209}Bi^{++}$ ions through a copper mesh mask with the cell size of $40\,\mu$m at energy $E = 72$ keV, current density $J = 5\,\mu A/cm^2$ and dose $D = 6.2 \cdot 10^{15}$ ion/cm^2. During ion implantation, swelling of the Bi:PGe layer occurred in unmasked areas of irradiated c-Ge. Formation of periodic Bi:PGe microstructures on the c-Ge surface was controlled by optical, electron and probe microscopy. The diffraction grating efficiency was shown by probing it with helium-neon laser radiation.

Keywords: nanoporous germanium, ion implantation, diffraction grating.

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To manifest various optical effects in modern Ge-based photonic devices such as solar cells [1], optoelectronic converters [2], photodiodes [3], photodetectors [4], etc., surface microstructuring is used. Among such thin-film microstructures there are absorption enhancers [5], anti-reflective coatings [6], and various diffractive elements [7,8].

Thin-film diffractive optical elements could be created based on layers of nanoporous Ge (PGe) [9]. In literature, PGe layers are conventionally referred to as „black Ge“ [10]. Paper [10] proposes a technique for creating PGe-layer-based diffraction gratings by imprinting. For this purpose, a periodic relief is formed on the surface of a hard-material master stamp by conventional lithography. Then the master stamp with the preset microstructure is applied to the Ge substrate containing a PGe layer pre-fabricated by some appropriate method. After that, the master stamp is pressed (imprinted) into the PGe layer. Under the applied pressure, the nanoporous layer undergoes selective mechanical deformation (or crushing) in localized microstructured regions. Thus, this technique involves several technological operations and does not allow for creating diffraction gratings in a single technological cycle.

One of the promising methods for fabrication PGe layers on the surface of single-crystal (c-Ge) or amorphous (a-Ge) substrates is ion implantation [11]. At the same time, papers report on fabricating periodic diffraction microstructures by irradiation with various ions through masks on such dielectric substrates as diamond (B^+) [12], polymer (Ag^+) [13], glass (He^+, N^+, Ag^+, Au^+) [14–16] and LiF (Cu^+, Ag^+) [17]. Earlier no diffraction gratings based on porous media were created by ion irradiation through masks. The goal of this study was to examine by Bi^{++} the possibility of forming an optical diffraction periodic microstructure by ion implantation through a mask in a single technological cycle simultaneously with creating ordered Bi:PGe fragments as the grating elements.

The Bi:PGe layers may be obtained by the method of focused ion beams in the electron microscope column [18]. However, the processed sample areas are of about only a few micrometers. Therefore, this approach cannot be efficiently used in practice to create large-scale (e. g. centimeter-scale) periodic diffractive elements.

Note also that interest in the Bi-Ge alloys and microstructures based on them is caused by the prospects for using them as anodes for magnesium-ion batteries [19].

To create a PGe-based diffraction grating, a 0.5 mm thick (111) c-Ge substrate (GDGI-45) was subjected to ion implantation. Irradiation was performed with doubly charged ions Bi^{++} with $E = 72$ keV, $D = 6.2 \cdot 10^{15}$ ion/cm^2 and $J = 5\,\mu A/cm^2$ by ion accelerator ILU-3 through a surface mask which was a copper grid with the square cell size of $40\,\mu$m. Local morphology and surface structure of the implanted c-Ge were studied with scanning electron microscope (SEM) Merlin (Carl Zeiss) at the accelerating voltage of 5 kV and current density of 300 pA, and also with scanning probe microscope (SPM) Dimension FastScan (Bruker) by the quantitative nanomechanical mapping method. Optical characterization of the fabricated gratings was performed using optical microscope Polar-1 (Mikromed). Optical diffraction patterns were obtained by probing the grating with a helium-neon laser at the wavelength of 632.8 nm.

Nonuniform distribution of implanted ions in the near-surface region of Ge irradiated with the $E = 72$-keV Bi^{++} ions was simulated using program code DYNA whose physical calculation principles are described in the work [20]. The program code accounts for dynamic variations in the surface layer chemical composition, which are caused due to the effects of paired collisions of accelerated ions with

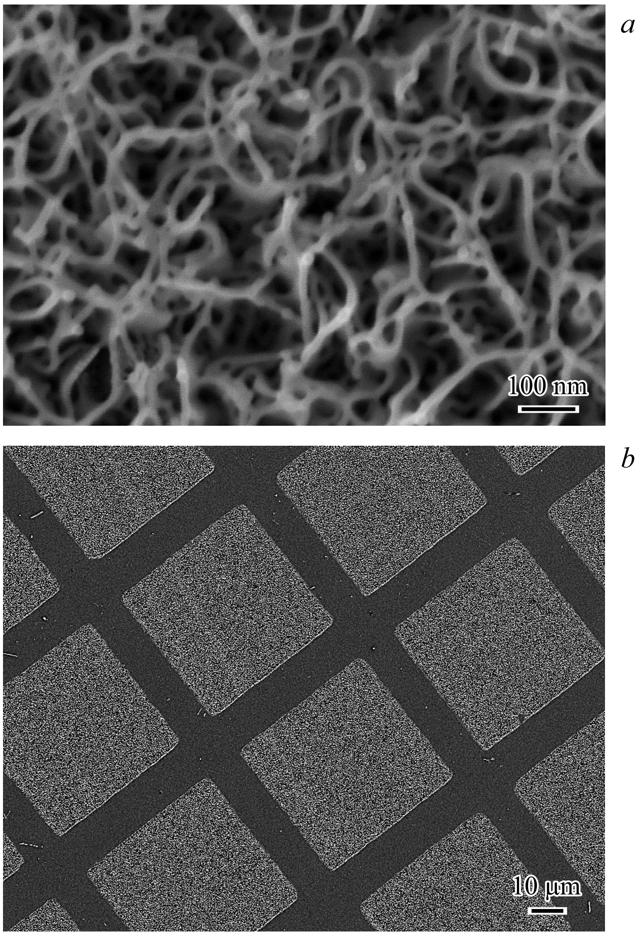

Figure 1. *a* — SEM image of the c-Ge surface implanted with Bi^{++} ions with $E = 72$ keV, $J = 5\,\mu$A/cm^2 and $D = 6.2 \cdot 10^{15}$ ion/cm^2. *b* — SEM image of the microstructured Bi:PGe layer formed by ion implantation.

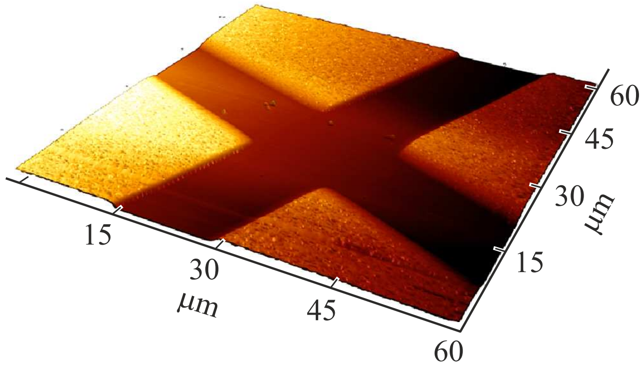

Figure 2. SPM image of the c-Ge surface implanted with Bi^{++} ions with $E = 72$ keV, $J = 5\,\mu$A/cm^2 and $D = 6.2 \cdot 10^{15}$ ion/cm^2.

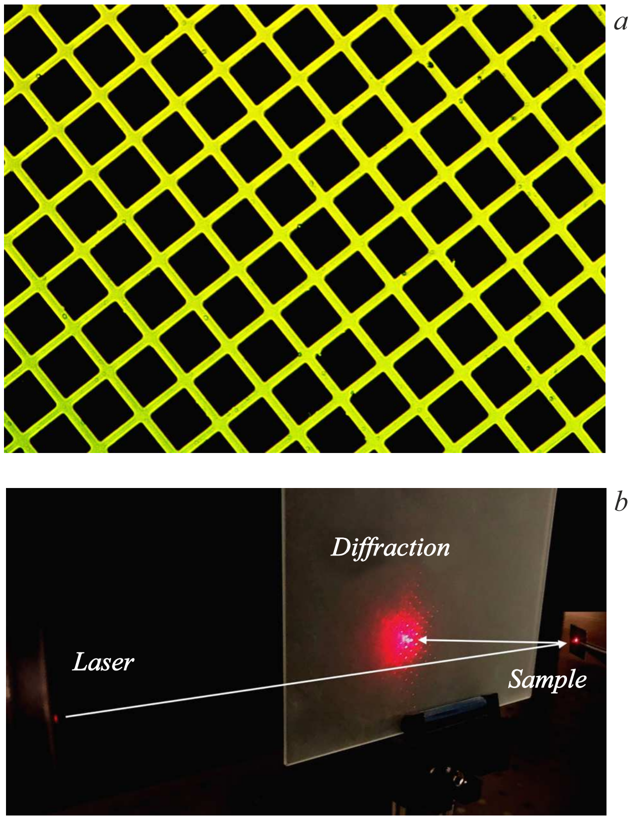

Figure 3. *a* — optical-microscope image of the microstructured Bi:PGe layer. The grating cell size is $40\,\mu$m. *b* — the displayed scattering pattern observed in the reflection mode from the diffraction grating by probing with a helium-neon laser.

irradiated matrix atoms, as well as of their sputtering. The simulation shown that by irradiation the Bi^{++} ions should be distributed Gaussian-wise in the Ge bulk from the surface with the maximum at the depth of $R_p \sim 21.8$ and ion range straggle of $\Delta R_p \sim 7.6$ nm. The calculated doped layer thickness $h = R_p + 2\Delta R_p$ is about 37 nm.

Fig. 1, *a* presents a SEM image of the surface for implanted Bi:PGe sample, which shows that the surface is a spongy-structured nanoporous layer consisting of intertwined Ge nanowires with ~ 10 nm of average diameter. The periodic structure formed by irradiation through a mask is shown in the SEM image in Fig. 1, *b*. The periodic microstructure consists of alternating light square cells corresponding to the implanted sample surface areas with the layered Bi:PGe structure, which are separated by smooth strips (dark areas) of unirradiated c-Ge. The size of the implanted area sides matches the mask cell size of $40\,\mu$m.

To additionally characterize the Bi:PGe sample structure, SPM measurements were performed; their results are shown in Fig. 2. The dark crosshair area refers to the initial c-Ge substrate surface which was covered by a mask during implantation. The figure shows that, under the given implantation conditions, the surface becomes considerably swollen (the volume of irradiated Bi:PGe increases relative to initial Ge), due to which a step gets formed. The swelling PGe layer height measured along the surface profile is about

100–110 nm, which, apparently, determines the effective working thickness of the anti-reflective optical coating.

Periodic surface microstructures on the c-Ge substrate implanted with Bi^{++} ions through a mask were examined with the optical microscope (Fig. 3, a). The entire sample surface about a centimeter in size is an ordered square-cell grid. Dark square cells correspond to the implanted Bi:PGe regions, light strips consist of c-Ge. Such periodic structures may play the role of photonic crystals and diffractive optical elements. As an illustration, Fig. 3, b presents a diffraction pattern observed by probing in reflection a periodically microstructured Bi:PGe-based element with the helium-neon laser. Obviously, it is possible to control the Ge structure optical and diffraction elements by manipulating the ion implantation modes thus changing the Ge structure, and by utilizing the effective refractive index of individual Bi:PGe regions in the grating.

Thus, in this paper it was considered the process of low-energy high-dose implantation of Bi^{++} ions into the c-Ge substrate through a surface mask and present a new technique for creating a diffraction grating based on periodic elements from the Bi:PGe (black germanium) spongy layer consisting of intertwined nanowires. As a result, an optical diffraction microstructure has been fabricated on the c-Ge surface whose phase contrast is provided by the Bi:PGe and c-Ge- regions.

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Conflict of interests

The authors declare that they have no conflict of interests.

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