08.1

Creation of an antireflection coating for the optical range based on a nanoporous germanium layer formed by implantation with indium ions

© A.L. Stepanov, V.I. Nuzhdin, V.F. Valeev, D.A. Konovalov, A.M. Rogov

Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, Kazan, Russia
E-mail: aanstep@gmail.com

The possibility of using a nanoporous Ge layer formed by implantation with ^{115}In$^+$ ions on a monocrystal c-Ge substrate as an antireflection optical coating (In:PGe) was studied. For this purpose, ion implantation of c-Ge wafers was performed at an energy $E = 30\,\text{keV}$, current density in the ion beam $J = 5\,\mu\text{A/cm}^2$, and dose $D = 1.8 \cdot 10^{16}\,\text{ion/cm}^2$. It was shown that the fabricated In:PGe spongy layer, which consists of intertwining Ge nanowires, is characterized by a low reflectivity ($\sim 5\%$) in a wide optical spectral range of $250-1050\,\text{nm}$.

Keywords: nanoporous germanium, ion implantation, antireflection optical coating.

Germanium, which is a semiconducting material with a high charge mobility and substantial absorption in the visible range, is presently used in practice to fabricate optical and optoelectronic devices, such as image sensors, photodetectors, solar cells, etc. [1–3]. However, owing to their high refractive index (> 4 in visible and near-infrared regions), Ge layers in photodetectors exhibit intense Fresnel optical reflection, which reduces the number of absorbed photons dramatically and, consequently, lowers the efficiency of optoelectronic devices. Various methods are used to suppress reflection off Ge layers. For example, a continuous multilayer interference thin-film antireflection coating may be applied to the photodetector surface to enhance the absorption of working materials. It was demonstrated the works [4,5] that this approach has a drawback: the reflectivity of working surfaces depends strongly on the incidence angle and the wavelength of light, and „favorable" interference manifests itself only in limited spectral ranges. Various nano- and microstructured surface Ge layers (so-called black Ge layers) produced in different ways were proposed as an alternative to continuous multilayer coatings to suppress optical reflection off Ge in a wide spectral range [6]. Apparently, one of the first techniques for fabrication of black Ge layers was presented the work [7], where a black surface consisting of Ge nanowires was formed by etching an amorphous a-Ge film in hydrogen peroxide H_2O_2. Similar microstructured surface Ge layers were prepared in the process of Ni-catalyzed growth from the vapor phase [8]. Black surface Ge layers based on periodic conical microstructures was also grown the work [9] by laser interference etching of c-Ge substrates. Another technique of this kind was etching in inductively coupled plasma [10], which provides an opportunity to fabricate Ge layers consisting of vertical pointed needles up to several tens of micrometers in length.

A „clean" vacuum ion-induced implantation technique, which relies on sputtering of the surface of a Ge target by a beam of fairly light ^{84}Kr$^+$ ions with relatively high energies $E = 100\,\text{keV}$ and doses up to $D = 3 \cdot 10^{18}\,\text{ion/cm}^2$ incident at a given angle, was proposed relatively recently [11] as a means to fabricate nanostructured porous Ge (PGe) layers on the surface of monocrystal c-Ge substrates. Following ion implantation, wave-like nanosized patterns, which become apparent sooner as the beam incidence angle increases, were formed on the c-Ge surface. It was demonstrated that a change in the c-Ge surface morphology translates into a reduction in the optical reflectivity of samples. However, the produced PGe layers formed by ^{84}Kr$^+$ ion implantation are rather thick ($\sim 100\,\text{nm}$) and are thus not suitable for ultra-compact photodetectors. Such ultra-compact photoelectronic devices with a reduced mass (down to a fraction of a gram with individual structural layers having a thickness of several nanometers) are much needed at present in the production of compact unmanned aerial vehicles, weather balloons, and satellites with a mass below $10\,\text{kg}$ to increase their flight duration and flying distance.

The possibility of fabrication of thin PGe layers in the process of high-dose low-energy implantation of c-Ge with various ions of transition metals was demonstrated the works [12,13]. It is expected that the use of heavier ions at lower energies (compared to the case of ^{84}Kr$^+$) should provide an opportunity to create thin antireflection optical PGe coatings. This is the reason why the present study is focused on examining the possibility of fabrication of low-reflection PGe layers by implantation with rather heavy ^{115}In$^+$ ions into a c-Ge surface. In earlier studies, the implantation of c-Ge substrates with ^{115}In$^+$ ions was performed at low doses mostly with the aim of producing specific electron impurity levels without altering the Ge surface morphology [14].
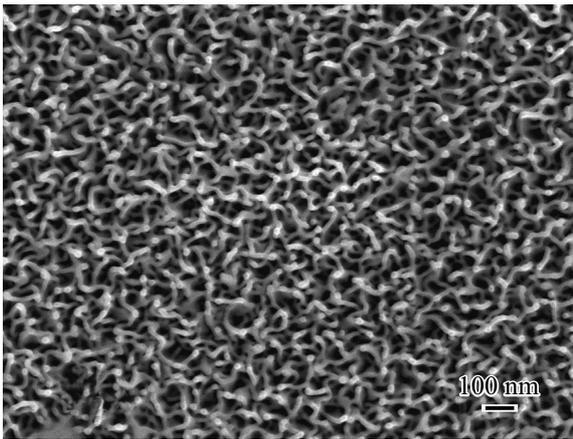
Figure 1. SEM image of the c-Ge surface implanted with ^{115}In$^+$ ions at $E = 30\,\text{keV}$, $J = 5\,\mu\text{A/cm}^2$, and $D = 1.8 \cdot 10^{16}$ ion/cm^2.

Smooth polished (111) c-Ge plate with a thickness of 0.5 mm was used as substrate for ion implantation in the experiment. The parameters of ^{115}In$^+$ ion implantation were as follows: $E = 30\,\text{keV}$, $D = 1.8 \cdot 10^{16}$ ion/cm^2, and $J = 5\,\mu\text{A/cm}^2$. An ILU-3 ion accelerator was used, and the substrate was kept at room temperature. The sample surface morphology was examined with a Merlin (Carl Zeiss) scanning electron microscope (SEM), the stage of which could be tilted by a given angle, at an accelerating voltage of 5 kV and a current density of 300 pA. Specular optical reflection spectra of samples in the range of $250-1050$ nm were measured with an AvaSpec-2048 (Avantes) waveguide spectrometer. Reflection spectra were also analysed in the same spectral range with the use of an AvaSphere-50-REFL (Avantes) integrating sphere to estimate the scattering of light off the sample surface backward from the direction of incidence.

Impurity distribution profiles in samples subjected to ion implantation were modeled using SRIM-2013 [15]. The obtained results reveal that the distribution of implanted ^{115}In$^+$ ions in Ge is characterized by a Gaussian curve with maximum at a depth of ~ 14.6 nm and a straggle of ~ 6.7 nm. Therefore, the doped layer thickness estimated with the effect of surface sputtering in the course of implantation taken into account is on the order of 20 nm. This value agrees with the results of SEM observations of the cross section at the end cleave of a sample at an angle of 40° to sample surface.

Figure 1 shows the SEM image of an In:PGe sample. It can be seen that the implanted surface is a spongy layer composed of intertwined Ge nanowires with an average diameter of ~ 10 nm.

Figure 2 presents the optical reflection spectra of the initial c-Ge substrate and an In:PGe sample implanted with ions. The c-Ge substrate spectrum demonstrates bands with their maxima at 276, 564, and 820 nm, which are derermened by intraband and interband electron transitions in c-Ge (this was already measured and characterized

theoretically in the case of polished bulk Ge surfaces the work [16]). It was reported the papaers [17,18] that the degree of Ge crystallinity is associated with the intensity of the band at 276 nm. Reflection bands with maxima at 276 and 564 nm vanish following the implantation of ^{115}In$^+$ ions into the c-Ge substrate (Fig. 2). This is indicative of amorphization of the sample surface and the formation of an In:PGe layer (Fig. 2). An integral suppression of reflection after amorphization of the surface of Ge implanted with ^{59}Ni$^+$ ions was also observed the work [19], although the Ge surface morphology wherein was found to remain unchanged. Therefore, it could be note an additional crucial reason for the redaction of In:PGe reflection: intense Rayleigh scattering of light by microstructures that, as was discussed the papers [7–10], leads to darkening of the sample. An In:PGe layer consisting of intertwined nanowires is produced as a result of implantation with ^{115}In$^+$ ions. This results in suppression of reflectivity (below 5%) of the sample within a wide spectral range. Reflection spectra were measured with an integrating sphere in order to estimate the possibility of scattering of light off the In:PGe sample backward from the direction of incidence. The reflectance measured by this way was found to remain very low (below 1%) throughout the entire studied spectral range. This fact allows to conclude that the optical absorption by an antireflection In:PGe coating is enhanced apparently due to the scattering of light within porous structures, which confine photons in the layer. A similar mechanism is assumed to affect the properties of various nanostructured materials [20,21].

Thus, it was demonstrated that an antireflection optical coating based on a thin (~ 20 nm) spongy layer of nanoporous germanium (black Ge), which is composed of intertwined nanowires, may be formed on the surface of a c-Ge substrate by low-energy high-dose implantation with ^{115}In$^+$ ions. The fabricated nanoporous Ge layer is characterized by low reflectivity ($\sim 5\%$) within a wide
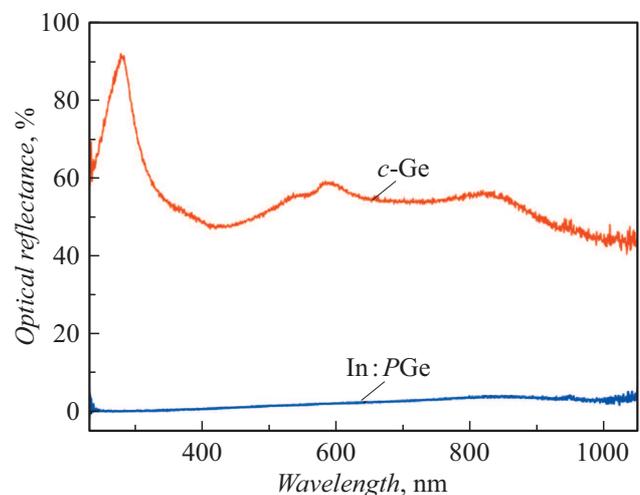
Figure 2. Optical reflection spectra of the initial polished c-Ge substrate and the antireflection coating based on an In:PGe layer.

spectral range of $250-1050$ nm. This antireflection coating may be used to raise the efficiency of optical and increase the overall photosensitivity of Ge photodetectors and solar cells.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] R. Kaufmann, G. Isella, A. Sanchez-Amores, S. Neukom, A. Neels, L. Neumann, A. Brenzikofer, A. Domman, C. Urban, H. von Kanel, J. Appl. Phys., **110**, 023107 (2011). DOI: 10.1063/1.3608245

[2] L. Tang, S.E. Kocabas, S. Latif, A.K. Okyay, D.S. Ly-Gagnon, K.C. Sarawat, D.A.B. Miller, Nat. Photonics, **2**, 226 (2008). DOI: 10.1038/nphoton.2008.30

[3] N.E. Posthuma, J. van der Heide, G. Flamand, J. Poortmans, IEEE Trans. Electron. Dev., **54**, 1210 (2007). DOI: 10.1109/TED.2007.894610

[4] H.K. Raut, V.A. Ganesh, A.S. Nair, S. Ramakrishna, Energy Environ. Sci., **4**, 3779 (2011). DOI: 10.1039/c1ee01297e

[5] N. Shanmugam, R. Pugazhendhi, R.M. Elavarasan, P. Kasiviswanathan, N. Das, Energies, **13**, 2631 (2020). DOI: 10.3390/en13102631

[6] S.B. Khan, H. Wu, C. Pan, Z. Zhang, Res. Rev.: J. Mater. Sci., **5**, 36 (2017). DOI: 10.4172/2321-6212.1000192

[7] L.R. Gilbert, R. Messier, R. Roy, Thin Solid Films, **54**, 149 (1978). DOI: 10.1016/0040-6090(78)90191-8

[8] L.R. Chueh, Z. Fan, K. Takei, H. Ko, R. Karadia, A.A. Rathore, N. Miller, K. Yu, M. Wu, E.E. Haller, A. Javey, Nano Lett., **10**, 520 (2010). DOI: 10.1021/nl903366z

[9] J.W. Leem, Y.P. Kim, J.S. Yu, J. Opt. Soc. Am. B, **29**, 357 (2012). DOI: 10.1364/JOSAB.29.000357

[10] S. Schicho, A. Jaouad, C. Sellmer, D. Morris, V. Aimez, R. Ares, Mater. Lett., **94**, 86 (2013). DOI: 10.1016/j.matlet.2012.12.014

[11] D.P. Datta, T. Som, Solar Energy, **223**, 367 (2021). DOI: 0.1016/j.solener.2021.05.016

[12] A.M. Rogov, V.I. Nuzhdin, V.F. Valeev, A.L. Stepanov, Compos. Commun., **19**, 6 (2020). DOI: 10.1016/j.coco.2020.01.002

[13] A.L. Stepanov, V.I. Nuzhdin, A.M. Rogov, V.V. Vorob'ev, *Formirovanie sloev poristogo kremnija i germanija s metallicheskimi nanochasticami* (Kazan. Nauchn. Tesntr Ross. Akad. Nauk, Kazan', 2019) (in Russian).

[14] F.D. Auret, P.J.J. van Rensburg, M. Hayes, J.M. Nel, W.E. Meyer, S. Decoster, V. Matias, A. Vantomme, Appl. Phys. Lett., **89**, 152123 (2006). DOI: 10.1063/1.2360922

[15] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, Nucl. Instrum. Meth. Phys. Res. B, **268**, 1818 (2010). DOI: 0.1016/j.nimb.2010.02.091

[16] J. Tauc, Progr. Semiconductors, **9**, 89 (1965).

[17] T.M. Donovan, W.E. Spicer, J.M. Bennett, E.J. Ashley, Phys. Rev. B, **2**, 397 (1970). DOI: 10.1103/PhysRevB.2.397

[18] H. Liu, S. Li, P. Sun, X. Yang, D. Liu, Y. Ji, F. Zhang, D. Chen, Y. Cui, Mater. Sci. Semicond. Process., **83**, 58 (2018). DOI: 10.1016/j.mssp.2018.04.019

[19] K.L. Bhatia, P. Singh, M. Singh, N. Kishore, N.C. Mehra, D. Kanjilal, Nucl. Instrum. Meth. Phys. Res. B, **94**, 379 (1994). DOI: 10.1016/0168-583X(94)95412-7

[20] K. Chen, J. Isometsa, T.P. Pasanen, V. Vahanissi, H. Savin, Nanotechnology, **32**, 35301 (2021). DOI: 10.1088/1361-6528/abbeac

[21] C. Ji, W. Liu, Y. Bao, X. Chen, G. Yang, B. Wei, F. Yang, X. Wang, Photonics, **9**, 906 (2022). DOI: 10.3390/photonics9120906