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Antireflection optical coatings formed by implantation of Ge with In$^+$ ions

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Fabrication of nanoporous Ge layers by implantation of monocrystalline *c*-Ge substrate with ^{115}In$^+$ ions for an antireflection optical coating was studied. Ion implantation of Ge wafers was carried out at energy E = 30 keV, current density J = 5 μA/cm^2 and doses D = 1.8·10^{15} - 7.2·10^{16} ion/cm^2. The surface morphology of the implanted samples was studied by scanning electron microscopy and the antireflection properties were analyzed by optical reflection spectroscopy. It is shown that the nanoporous In:PGe layers with spongy structures, consisting of intertwining Ge nanowires formed at highest values of D = 1.9-7.2·10^{16} ion/cm^2 is characterized by very low reflectivity (~5%) in a wide optical spectral range of 200-1050 nm.

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1. Introduction

Nano- and microstructured Ge layers are used in practice as effective antireflection optical coatings to increase the absorption capacity of various Ge-based optoelectronic devices such as photodetectors, video- and photosensors, solar cells, etc. [1-4]. Antireflection structured Ge layers are referred in the literature as “black Ge” [5–9]. Various chemical and physical techniques were proposed to create black Ge layers. Apparently, one of the first such technologies was proposed in 1978 in the work [7], in which a black antireflection surface consisting of Ge nanowires was formed after etching sputtered non-crystalline Ge films in hydrogen peroxide H_2O_2. Similar nanoneedle-like black Ge surfaces were created by using a Ni-catalysed vapor deposition process [8]. Also, a lithography-free self-organized coupled plasma etching was selected for constriction of vertical tapered Ge needles [5]. In the work [9], laser etching of Ge in SF_6 atmosphere was applied to fabricate conical microstructures with nanospikes on top by varying laser intensity and number of pulses.

In contrast to the given technology examples of chemical approaches for fabrication of antireflection structured Ge layers, the physical vacuum technology of ion implantation is of particular interest. Relatively recently, in order to create an antireflection coating made of porous Ge layer (PGe) on the surface of *c*-Ge substrates, it was proposed to perform implantation with relatively light ^{84}Kr$^+$ ions of an inert gas at sufficiently high energy E = 100 keV and dose D = 3.0·10^{18} ion /cm^2 [10]. As a result, wavy nanosized patterned structures were formed on the *c*-Ge surface, the shape of which is determined by different angles of incidence of the ion beam. It was found that a change in the surface morphology of implanted *c*-Ge in such situations leads to a decrease in the optical reflection.

Much earlier in the works [11, 12], some light darkening of the *c*-Ge substrate surfaces was visually observed after rathe low doses (D = 2.0-5.0·10^{15} ion/cm^2) implantation with metal ions ^{115}In$^+$ at high values of E = 120 keV. In this case, the implantation-induced light darkening of the samples was correlated with the amorphization of the implanted Ge substrate surface. However, no spectral measurements of optical reflection from implanted layers were carried out. It should also be noted that the implantation of *c*-Ge with ^{115}In$^+$ ions at lower D = 2.0·10^{11} ion/cm^2 and high E = 160 keV did not lead to sample darkening and such D was used in practice only to create a dopant in Ge and increase the number of current carriers [13].

In the work [14], the formation of thin PGe layers after high-dose low-energy implantation of *c*-Ge with various transition metal ions was demonstrated. Different morphological structures of PGe implanted surfaces were observed by electron microscopy. Now, it is expected that the use of heavier metal ions at a noticeably lower E compared to, for example, the case of ^{84}Kr$^+$ [10], will make it possible to fabricate thin effective antireflection optical PGe coatings. Therefore, the present article is devoted to a detailed study of creating some low-reflecting In:PGe layers by implantation of *c*-Ge substrates with rather heavy ^{115}In$^+$ ions.

2. Experimental

Polished monocrystalline *c*-Ge wafers with crystallographic orientation (111) were selected as substrates for ion implantation, which was carried out by ^{115}In$^+$ ions with E = 30 keV, D from 1.8·10^{15} to 7.2·10^{16}

ion/cm^2 at $J = 5$ μA/cm^2 using the ILU-3 ion implanter at a normal angle of ion beam incidence to the *c*-Ge surface at room temperature. The analysis of the surface morphology was carried out by a scanning electron microscope (SEM) Merlin (Carl Zeiss) at an accelerating voltage of 5 kV and a current density of 300 pA. Estimation of antireflection properties of formed In:PGe layers were realized by measurements of optical reflection spectra with an AvaSpec 2048 (Avantes) spectrometer in the range from 200 to 1050 nm.

3. Results and discussion

The impurity distribution profiles in the sample volume during ion implantation were modeled using the SRIM-2013 computer program. The results show that the implanted ^{115}In$^+$ ions positioned in Ge according to a Gaussian statistical curve with a maximum at an ion range of ~ 14.6 nm and a straggle of ~ 6.7 nm. Therefore, the thickness of the doped layer could be estimated to be about ~ 20 nm.

SEM-images of In:PGe samples formed by implantation with ^{115}In$^+$ ions for various values of D are shown in Fig. 1. As could be seen from the figure, with increasing D the morphology of the surface layers changes. Starting from a lower considered value $D = 1.8 \cdot 10^{15}$ ion/cm^2, the flat polished *c*-Ge substrate, which the SEM-image was shown in the work [15], after implantation becomes porous with the In:PGe honeycomb structure (Fig. 1a). Similar honeycomb In:PGe layers were previously observed in the case of ion implantation at higher values of $E = 120$ keV and $D = 5.0 \cdot 10^{15}$ ion/cm^2 [11, 12]. The formation of a PGe honeycomb structure was also created on *c*-Ge substrate after implantation with significantly lighter ions ^{52}Cr$^+$, but with a higher $D = 5.0 \cdot 10^{16}$ ion/cm^2 ($E = 40$ keV) [14].

When D increases up to $3.6 \cdot 10^{15}$ ion/cm^2, the In:PGe honeycomb structure transforms into a labyrinth layer (Fig. 1b). After implantation with ^{115}In$^+$ ions at higher D over $1.3 \cdot 10^{16}$ ion/cm^2, the In:PGe structure again undergoes changes and becomes a spongy structure, consisting of intertwining Ge nanowires (Fig. 1c). Note that in the range D from $1.3 \cdot 10^{16}$ to $7.2 \cdot 10^{16}$ ion/cm^2 used in this work, the In:PGe morphology remains qualitatively of the similar spongy type, differing from each other in the diameter of the nanowires and the volume of voids between them in the implanted porous layer. The size of nanowire diameters and the distance between them in In:PGe increase with rising of D, as could be seen from the comparison of the corresponding In:PGe SEM-images (Figs. 1c and 1d).

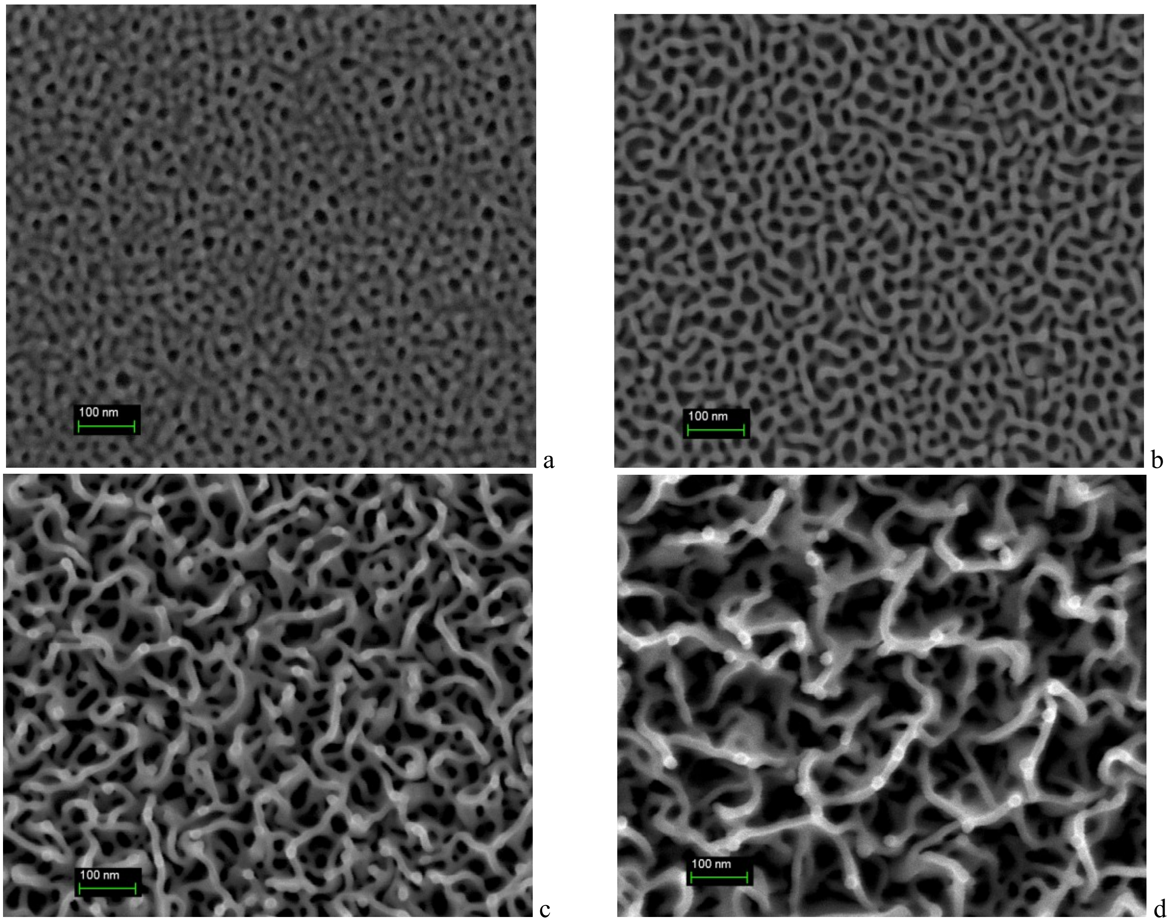

Fig. 1. SEM-images of c-Ge sample surfaces formed by implantation with ^{115}In$^+$ ions at $E = 30$ keV, $J = 5$ μA/cm^2 for various D: (a) $1.8 \cdot 10^{15}$; (b) $3.6 \cdot 10^{15}$; (c) $1.3 \cdot 10^{16}$ and (d) $1.9 \cdot 10^{16}$ ion/cm^2

The formation of a spongy layer with nanowires was also observed for *c*-Ge substrates after implantation with heavy $^{108}Ag^+$ and $^{122}Sb^+$ ions [14]. A decrease of nanowire diameters in consistence with an increase in the mass of the implanted ion was concluded for these samples. Note, that in the works [11, 12] the study of implantation with $^{115}In^+$ ions was limited to a narrow interval D = 2.0-5.0·10^{15} ion/cm^2 only.

Nevertheless, it was shown, that the formation of In:PGe is preceded by amorphization of the near-surface implanted layer for $D \sim 10^{15}$ ion/cm^2, but it is appreciably lower value of the critical D for nanopores formation. Therefore, it could be concluded that the observed implanted In:PGe layers in present work also is amorphous in contrast to PGe layers with nanowires of a crystalline structure formed by electrochemical methods [16].

Additionally, it should be mentioned the results obtained in the work [17, 18], in which high-dose implantation of *c*-Ge with $^{115}In^+$ ions was carried out up to D = 5.4·10^{16} ion/cm^2 at E = 700 – 3400 keV and a high substrate temperature T_{subst} = 250 °C to avoid amorphization of the implanted layer. In some cases, the samples were thermally annealed. For the given conditions of implantation and annealing the surface In:PGe layer was not formed, since the average penetration range of $^{115}In^+$ ions is on the order of 200–1200 nm for various E, and so In impurity were accumulated in a large depth in irradiated samples. When the values D = 3.6·10^{15} ion/cm^2 (> 0.6 at. % of In in Ge) were exceeded, the formation of In nanoparticles with an average size of 10 nm was detected by transmission electron microscopy in the volume of the *c*-Ge substrate. Therefore, it could be concluded that in all In:PGe structures formed in present work at a significantly low E and high D metal In nanoparticles were also synthesized.

As informed in the introduction, the optical properties of In:PGe samples fabricated by ion implantation were not previously studied in full measure. The optical reflection spectra of the In:PGe samples as a function of D and, for comparison, for the nonimplanted *c*-Ge substrate are presented in Fig. 2. The spectrum of the *c*-Ge substrate is characterized by selective bands with maxima at 276, 564 and 820 nm, determined by intraband and interband electronic transitions in *c*-Ge as discussed in the work [19]. Practically important that the degree of crystallinity of Ge is identified by the intensity of the bands at 276 and 564 nm. As follows from Fig. 2 (curves a–d), with increasing D a monotonic decrease of the reflection intensities of these bands is observed. It could be due to the amorphization of the implanted In:PGe. Similar reflection reduction effect at 276 and 564 nm during surface amorphization of Ge implanted with light ions $^{59}Ni^+$ (E = 60 MeV, D = 5.0·10^{13} - 8.0·10^{14} ion/cm^2) and $^{16}O^+$ (E = 45 keV, D = 1.0·10^{17} - 1.5·10^{18} ion/cm^2) without PGe formation was shown in the works [20, 21].

The decrease in the optical reflection of the Ge surface also occurs as a result of nano- and micro structuring, and corresponding intense Rayleigh light scattering from these structures [5-8]. From a comparison of the In:PGe surface microstructures (Fig. 1) and corresponding them optical reflection spectra (Fig. 2, curves a-d), it is possible to conclude that the development of a porous surface from a honeycomb structure to a spongy one with nanowires leads to a decrease of the reflection coefficient R over the considered spectral range from 200 to 1050 nm to values less than R = 5%. Thus, starting from D = 1.9·10^{16} ion/cm^2 the In:PGe sample get a saturated black color (black Ge). A further increase of D does not change the optical spectrum of dark In:PGe samples.

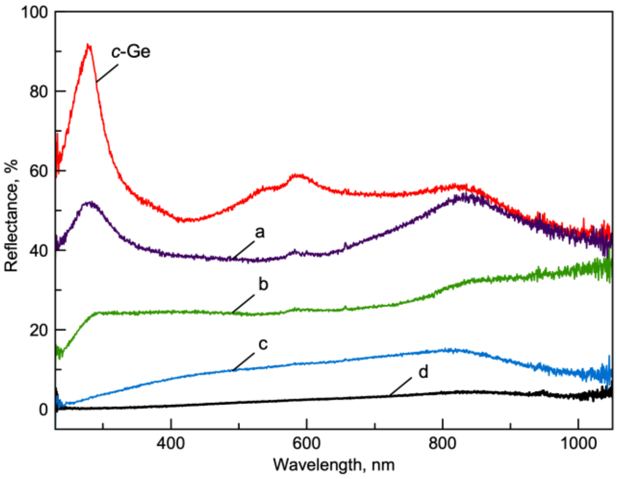

Fig. 2. Optical reflectance spectra of c-Ge substrate and c-Ge sample surfaces formed by implantation with $^{115}In^+$ *ions at* E *= 30 kev,* J *= 5 μA/cm*^{2} *for various D: (a) 1.8·10*^{15}*; (b) 3.6·10*^{15}*; (c) 1.3·10*^{16} *and (d) 1.9·10*^{16} *ion/cm*^{2} *(colour online)*

A similar integral decrease in the intensity of optical reflection with increasing D was also observed for spongy Ag:PGe layers consisting of intertwining nanowires formed by implantation with $^{108}Ag^+$ ions at E = 30 keV and D = 6.2·10^{16} - 1.5·10^{17} ion/cm^2 [19]. However, for Ag:PGe layer in a wide part of the spectral range of 400–1050 nm, the coefficient R was not higher than 20% in comparison to In:PGe (Fig. 2, curve d). The color of Ag:PGe sample turned out to be dark gray during visual observation. Despite the qualitative similarity between the structures of the In:PGe and Ag:PGe layers observed in SEM-images, there are certain granulometry differences between them. The size of nanowire diameters in In:PGe (Figs. 1c and 1d) are approximately two times smaller than in Ag:PGe samples [14, 15, 19]. In addition, it should be noted that an increase in the space between nanowires and their thinning in In:PGe (Figs. 1c and 1d) leads to a significant decrease of the integral optical absorption (Fig. 2, curves c, d). Thus, it could be concluded that, using the physical method of implantation of *c*-Ge wafers with $^{115}In^+$ ions at E = 30 keV and D = 1.9·10^{16} ion/cm^2, it is possible to form an effective antireflection optical coating over the total visible spectrum range. At the same time, the metal In nanoparticles present in the In:PGe layer structure. Such nanoparticles exhibits plasmonic optical absorption and reflection in vacuum with maximum near 200 nm [22], but they do not affect the integral reflection of the implanted In:PGe layers (Figs. 2 a-d), apparently due to the high refractive index of Ge and corresponding spectral smearing of selective plasmonic bands of In nanoparticles.

4. Conclusion

In the present work, it is shown that the method of low-energy high-dose implantation of a *c*-Ge substrate with ^{115}In$^+$ ions at E = 30 keV and D = 1.9-7.2·10^{16} ion/cm^2 could be useful to form an effective antireflection optical coating by a thin (~20 nm) a spongy layer of In:PGe consisting of intertwining nanowires (black Ge). The resulting In:PGe layer is characterized by low reflectivity (R ~ 5 %) in a wide optical spectral range from 200 to 1050 nm. The antireflection coating could serve to increase the efficiency of photon absorption and improve the overall light sensitivity in Ge photodetectors, sensors and solar cells based on them.

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References

[1] J. W. Leem, Y. M. Song, J. S. Yu, Opt. Express **19**, 26308 (2011).
[2] 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**, 23107 (2011).
[3] L. Tang, S. E. Kocabas, S. Latif, A. K. Okyay, D. S. Ly-Gagnon, K. C. Sarawat, D. A. B. Miller, Natur. Photonics **2**, 226 (2008).
[4] N. E. Posthuma, J. van der Heide, G. Flamand, J. Poortmans, IEEE Trans. Electron. Dev. **54**, 1210 (2007).
[5] S. Schicho, A. Jaouad, C. Sellmer, D. Morris, V. Aimez, R. Ares, Mater. Lett. **94**, 86 (2013).
[6] M. Steglich, T. Käsebier, E.-B. Kley, Appl. Phys. A **122**, 836 (2016).
[7] L. R. Gilbert, R. Messier, R. Roy, Thin Solid Films **54**, 149 (1978).
[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).
[9] B. K. Nayak, M. C. Gupta, K. W. Kolasinski, Nanotechnology **18**, 195302 (2007).
[10] D. P. Datta, T. Som, Solar Energy **223**, 367 (2021).
[11] O. W. Holland, B. R. Appleton, J. Narayan, J. Appl. Phys. **54**, 2295 (1983).
[12] B. R. Appleton, O. W. Holland, D. B. Poker, J. Narayan, D. Fathy, Nucl. Instr. Meth. Phys. Res. B **7/8**, 639 (1985).
[13] 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).
[14] A. M. Rogov, V. I. Nuzhdin, V. F. Valeev, A. L. Stepanov, Composites Comm. **19**, 6 (2020).
[15] A. L. Stepanov, B. F. Farrakhov, Ya. V. Fattakhov, A. M. Rogov, D. A. Konovalov, V. I. Nuzhdin, V. F. Valeev, Vacuum **186**, 1100 (2021).
[16] A. Pavlikov, A. Sharafutdinova, I. Gavrilin, V. Zaytsev, A. Dronov, S. Gavrilov, Phys. Stat. Sol A **218**, 2100245 (2021).
[17] R. Feng, F. Kremer, D. J. Sprouster, S. Mirzaei, S. Decoster, C. J. Glover, S. A. Medlig, S. P. Russo, M. C. Ridgway, J. Appl. Phys. **118**, 165701 (2015).
[18] R. Feng, F. Kremer, D. J. Sprouster, S. Mirzaei, S. Decoster, C. J. Glover, S. A. Medling, L. M. C. Pereira, S. P. Russo, M. C. Ridgway, Appl. Phys. Lett. **107**, 212101 (2015).
[19] A. L. Stepanov, A. M. Rogov, Opt. Commun. **474**, 126052 (2020).
[20] K. L. Bhatia, P. Singh, M. Singh, N. Kishore, N. C. Mehra, D. Kanjilal, Nucl. Instr. Meth. Phys. Res. B **94**, 379 (1994).
[21] Q.-C. Zhang, J. C. Kelly, M. J. Kenny, Nucl. Instr. Meth. Phys. Res. B **47**, 257 (1990).
[22] M. B. Ross, G. C. Schatz, J. Phys. Chem. C **118**, 12506 (2014).

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