ISSN 1027-5495. Functional Materials, 32, No.2 (2025), p. 184-189
doi:http://dx.doi.org/10.15407/fm32.02.184

Radiation-modified n-Ge and n-Si single crystals for IR equipment

S.V. Luniov, D.A. Zakharchuk, L.Yu. Zabrodotska

Lutsk National Technical University, 75 Lvivska Str., Lutsk 43018, Ukraine

Received December 4, 2024

IR absorption spectra for n-Ge and n-Si single crystals, irradiated by fast electron flows, were investigated at room temperature. Additional absorption bands in the long-wave IR range, which are associated with the created radiation defects, were identified in these spectra after irradiation. In particular, in germanium: the absorption band at 15 µm for the VO_iI_{2Ge} complex (vacancy-oxygen complex, two interstitial germanium atoms); in silicon: the absorption band at 12 µm for the A-center (vacancy-interstitial oxygen atom complex) and the A-center, modified by the phosphorus impurity (VO_iP complex), and the absorption band at 11.6 µm, which is associated with the C_iO_i complex (interstitial carbon-oxygen). The analysis of absorption spectra for the irradiated germanium and silicon single crystals and the calculations of the relative values of the photosensitivity coefficients for the obtained absorption bands show that the photosensitivity of these single crystals in the long-wave range of IR radiation increases with increasing the electron irradiation flow. This is due to an increase in the concentration of created radiation defects, which are absorption centres for IR radiation and, accordingly, determine the value of the photosensitivity coefficient. Electron-irradiated n-Ge and n-Si single crystals can be alternative materials to much more expensive and "cooled" narrow-gap semiconductor materials which are used in the devices controlling long-wave IR radiation.

Keywords: irradiated n-Ge and n-Si single crystals, radiation defects, photosensitivity coefficient, IR radiation.

Радіаційно-модифіковані монокристали n-Ge та n-Si для ІЧ-техніки. *С.В. Луньов, Д.А. Захарчук, Л.Ю. Забродоцька*

Для монокристалів n-Ge та n-Si, опромінених швидкими потоками електронів, було досліджено спектри ІЧ-поглинання при кімнатній температурі. В спектрах після опромінення були ідентифіковані додаткові смуги поглинання в довгохвильовому ІЧ-діапазоні, які пов'язанні з утвореними радіаційними дефектами. Зокрема, в германії: смуга поглинання при 15 мкм для комплексу VO_iI_{2Ge} (комплекс вакансія-кисень, два міжвузлових атоми германію); в кремнії: смуга поглинання при 12 мкм для А-центру (комплекс вакансія-міжвузловий атом кисню) та А-центру, модифікованому домішкою фосфору (комплекс VO_iP), смуга поглинання при 11,6 мкм, пов'язана з комплексом C_iO_i (міжвузловий вуглець-кисень). Аналіз спектрів поглинання для опромінених монокристалів германію та кремнію та проведених розрахунків відносних значень коефіцієнтів фоточутливості для одержаних смуг поглинання показує, що фоточутливість даних монокристалів в довгохвильовому діапазоні ІЧ-випромінювання зростає зі збільшенням потоку опромінення електронами. Це пов'язано зі збільшенням концентрації утворених радіаційних дефектів, які є центрами поглинання для ІЧ-випромінювання та відповідно визначають величину коефіцієнта фоточутливості. Опромінені електронами монокристали n-Ge та n-Si можуть бути альтернативними матеріалами до значно дорожчих та «охолоджувальних» вузькозонних напівпровідникових матеріалів, які використовуються в приладах контролю ІЧ-випромінювання довгохвильового діапазону.

1. Introduction

The currently well-developed technology for growing the silicon and germanium single crystals opens up prospects for using these semiconductor materials in modern electronics and sensors [1]. In particular, silicon and germanium photonics are now widely used in modern optoelectronic devices, information and communication technologies, sensors and energy, the development of new methods of quantum information theory, and biosensors [2-7]. In this regard, the efforts of many scientists and engineers are aimed at creating compact and high-performance components based on semiconductor chips, using already well-known technologies for manufacturing silicon and germanium microelectronic elements. The main method of modifying the electrical and optical properties of semiconductor materials, in particular silicon and germanium, is doping with various impurities [8, 9]. However, the use of this method is limited due to the low solubility of certain impurities in semiconductors. Modifying many physical properties of the complex compounds, such as the chalcogenide glasses or nanoporous ceramics of the spinel type $MgAl_2O_4$, is achieved by changing the chemical composition or defect structure of these materials [10–13]. The resulting complex compounds are often very heterogeneous in electrical and optical properties, which is a disadvantage of the practical application of these materials in the manufacture of electronic components based on them. These problems can be eliminated using radiation technologies. The ability of varying the energy, electron flow and irradiation temperature allows for wide control over the concentration, nature, and distribution of the created radiation defects in the material and, accordingly, the electrical, galvanomagnetic, optical, and photoelectric properties of semiconductors. New electronic devices and sensors can be manufactured based on semiconductor materials that have undergone additional radiation treatment.

Single-crystalline silicon and germanium are promising materials for photonics, in particular for the manufacture of IR radiation receivers [14–19]. However, to register infrared radiation of different ranges with such receivers, it is necessary to change the doping admixture and in most cases to cool the sensitive element to the temperature of liquid nitrogen or helium. In this regard, the use of radiation technologies will make it possible to create radiation defects in the volume of silicon and germanium that are photosensitive in the medium and long-wave range of IR radiation at room temperature. In works [20, 21], n-Si single crystals were obtained, that were subjected to ion implantation with boron ions at flows from 10^{13} cm^{-2} to $1 \cdot 10^{15}$ cm^{-2}, followed by annealing for 20 minutes at temperatures of 800–1000 °C. As a result of the treatment, silicon was obtained that is photosensitive in the near-IR region from 1.4 to 2.2 µm. The authors of [22] studied the effect of electron irradiation with an energy of 10 MeV, a flow of $\Omega=5 \cdot 10^{15}$ el./cm^2 with additional isothermal annealing of irradiated samples for 6 hours at the t=120 °C on the transformation of the IR absorption spectra of n-Ge single crystals at room temperature. It was established that an increase in photosensitivity of the investigated n-Ge single crystals, associated with the absorption band of 15 µm of the created radiation defects, will be observed during 4 hours of annealing.

Further annealing resulted in a decrease in the intensity of this absorption band. The authors of the work [23] studied the absorption spectra of n-Si single crystals irradiated by the electrons with an energy of 12 MeV and a flow of $\Omega=1 \cdot 10^{17}$ el./cm^2 in the temperature range of 10–300 K. Three bands at 11.3 µm, 11.6 µm, and 12 µm, which correspond to the created radiation defects, in the absorption spectra of irradiated silicon samples were identified. An increase in temperature led to a decrease in the intensity of these absorption bands. Only the absorption bands at 11.6 µm and 12 µm at room temperature were observed. In works [22, 23], absorption bands associated with created radiation defects, which belong to the long-wave range of infrared radiation, were observed for single crystals of germanium and silicon irradiated with electrons. IR detectors based on HgCdTe, PbSnTe solid solutions and microbolometers used in night vision devices, infrared sights, etc., work in this range [24]. Therefore, electron-irradiated germanium and silicon single crystals are promising materials for developing such IR devices based on them. For irradiated germanium and silicon single crystals, it is necessary to obtain the dependences of the absorption coefficients of IR radiation on the magnitude of electron irradiation flow for a more comprehensive study of the photosensitivity of such single crystals and to establish optimal conditions for their radiation treatment.

Therefore, the purpose of this work was to study the absorption spectra of n-Ge and n-Si single crystals irradiated by different flows of electrons at room temperature and to evaluate their photosensitivity associated with the created radiation defects.

2. Experimental results and theoretical calculations

The samples of germanium single crystals doped by the antimony impuritywith the concentration of $N_d=5\cdot10^{14}$ cm^{-3}, were irradiated by the electrons with an energy of 10 MeV and flows from $5\cdot10^{15}$ el./cm^2 to $5\cdot10^{16}$ el./cm^2. Silicon single crystals doped with phosphorus impurity at a concentration of $N_d=2.2\cdot10^{16}$ cm^{-3}, were irradiated by the electrons with an energy of 12 MeV and flows from $5\cdot10^{16}$ el./cm^2 to $3\cdot10^{17}$ el./cm^2. The concentrations of interstitial oxygen in unirradiated germanium and silicon single crystals were $8\cdot10^{15}$ cm^{-3} and $9\cdot10^{17}$ cm^{-3}, respectively, and the concentration of carbon in silicon was $6\cdot10^{16}$ cm^{-3}. These samples were irradiated at room temperature at a laboratory-research facility – M–30 microtrons in the Department of Photonuclear Processes of the Institute of Electronic Physics of the National Academy of Sciences of Ukraine. To achieve the required irradiation flow, the exposure time was determined taking into account the irradiation flow density $j=4\cdot10^{11}$ el./(cm$^2\cdot$s). Absorption spectra of irradiated n-Ge and n-Si samples were measured at room temperature on an IR-Fourier spectrophotometer IRAffinity–1S in the spectral range of 1.3–28 μm. Absorption spectra for irradiated n-Ge and n-Si single crystals are presented in Fig. 1 and Fig. 2.

As is known [25], the photosensitivity of the material is related to the absorption coefficient. The photosensitivity coefficient of the material is defined as

$$S = \frac{\Delta\sigma}{J} \quad (1)$$

where $\Delta\sigma = \sigma - \sigma_0$ is the photoconductivity, σ is the specific electrical conductivity of the semiconductor under illumination, σ_0 is the dark value of the specific electrical conductivity, J is the intensity of the light incident on the sample.

$$\Delta\sigma = B\cdot\alpha\cdot\phi, \quad (2)$$

where B is a constant that depends weakly on the light frequency, α is the absorption coefficient, $\phi = \frac{J}{h\nu}$ is the incident flow of photons.

Then

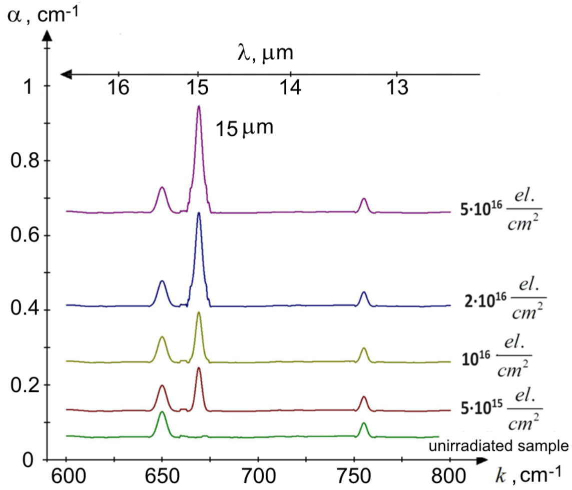

Fig. 1. Absorption spectra at room temperature for n-Ge single crystals irradiated by different electron flows.

$$S = \frac{B\cdot\alpha}{h\nu} = \frac{B\cdot\alpha\cdot\lambda}{hA} \quad (3)$$

The relative increasing the photosensitivity of the semiconductor in the case of light absorption by impurities or defects can be calculated as

$$\delta = \frac{S_{max}}{S} = \frac{\alpha_{max}}{\alpha}, \quad (4)$$

where α_{max}, α are the values of the absorption coefficients at the maximum and at the base of the absorption peak, which correspond to a certain doping impurity or defect.

Based on expression (4) and the obtained experimental results (Fig. 1 and Fig. 2), it is possible to calculate the relative increase in the photosensitivity of n-Ge and n-Si single crystals, caused by radiation defects created under the influence of electron irradiation. The results of such calculations are presented in Tables 1 and 2. As follows from Tables 1 and 2, the photosensitivity of irradiated n-Ge and n-Si single crystals for wavelengths of 11.6, 12, and 15 μm increases with increasing electron irradiation flow.

3. Results and Discussion

As follows from Fig. 1, a new absorption band at 669 cm^{-1} (15 μm) appears in the spectra of n-Ge samples irradiated by electrons. According to the data of works [26, 27], this band corresponds to the negatively charged state of the A-center (interstitial atom of oxygen-vacancy). In works [28, 29], we slightly refined the microstructure of this complex for the

Table 1. Relative values of photosensitivity for n-Ge single crystals irradiated by different flows of electrons with energy of 10 MeV.

Single crystal	Electron radiation flow Ω, el./cm^2	Relative increase in photosensitivity δ for a band 15 μm
n-Ge	$5\cdot10^{15}$	2.6
	$1\cdot10^{16}$	3.6
	$2\cdot10^{16}$	5.7
	$5\cdot10^{16}$	6.8

Table 2. Relative values of photosensitivity for n-Si single crystals irradiated by different flows of electrons with energy of 12 MeV.

Single crystal	Electron radiation flow Ω, el./cm^2	Relative increasing photosensitivity δ	
		Band 12 μm	Band 11.6 μm
n-Si	$5\cdot10^{16}$	1.4	1.4
	$1\cdot10^{17}$	2.4	2.3
	$2\cdot10^{17}$	2.8	2.4
	$3\cdot10^{17}$	3.3	2.5

same germanium single crystals irradiated by electrons, based on measurements of the Hall effect and solutions of electroneutrality equations. According to the data of these works, the created radiation defect is the A-center which is additionally modified by two interstitial germanium atoms (VO_iI_{2Ge} complex). As can be seen from Fig. 1, the intensity of the absorption band at 669 cm^{-1} for the VO_iI_{2Ge} complex and the area under the curve of the peak increase with increasing irradiation flow. This is explained by the increasing concentration of radiation defects belonging to VO_iI_{2Ge} complexes [28]. The absorption bands at 650 cm^{-1} and 755 cm^{-1} correspond to the absorption of IR radiation by optical phonons in germanium [30]. In the absorption spectra of electron-irradiated n-Si single crystals, two additional bands appear at 836 cm^{-1} (12 μm) and 865 cm^{-1} (11.6 μm) (Fig. 2). The absorption band at 836 cm^{-1} corresponds to the neutral state of the A-centre [31], and the band at 865 cm^{-1} corresponds to the C_iO_i complex (interstitial carbon-oxygen) [32]. According to the Watkins exchange mechanism, carbon is pushed by its own interstitials from site to site, creating a stable defect C_i under the influence of irradiation [33, 34]. Annealing of this defect occurs near room temperature by diffusion. When diffusing in the lattice, interstitial carbon effectively interacts with various impurities, creating many

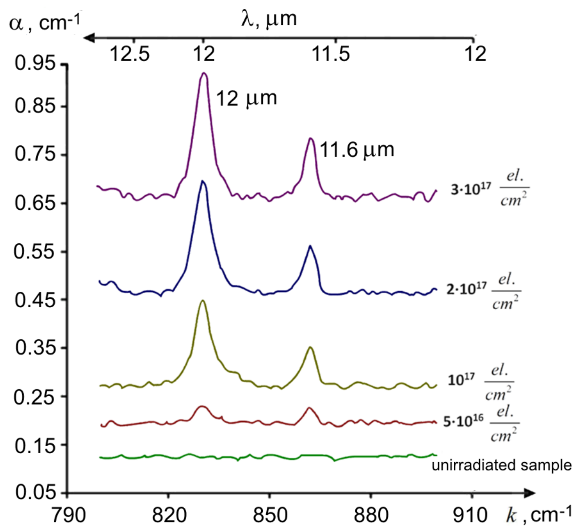

Fig. 2. Absorption spectra at room temperature for n-Si single crystals, irradiated by different electron flows.

different electrically active interstitial defects. In silicon grown by the Czochralski method, the most probable interaction is between interstitial carbon and interstitial oxygen, which leads to the creation of the C_iO_i complex. Also, as we have previously established in works [34, 35], under the electron irradiation, in the bulk of these n-Si single crystals, somewhat more complex radiation defects belonging to VO_iP complexes (complex of the vacancy, interstitial oxygen atom and atom of the alloying phosphorus impurity) are created in parallel with the well-studied A-centers in silicon [36]. As in germanium, a similar increase in the intensity of these bands and the area under curves of the peaks with the increasing electron irradiation flow is associated with an increase in the concentration of created radiation defects [34]. Moreover, A-centers and VO_iP complexes will be created more intensively in the bulk of the silicon sample with increasing irradiation flow. This is explained by the fact that the probability of quasi-chemical reactions with the creation of the A-centers and VO_iP complexes is greater than that of the C_iO_i complexes since the concentration of interstitial oxygen in the investigated silicon single crystals is more than an order of magnitude greater than the concentration of interstitial carbon.

According to the data in Tables 1 and 2, the change in the relative value of the photosensitivity $\Delta\delta/\Delta\Omega$ for n-Ge a C_i nd n-Si with an increase in the electron irradiation flow for absorption bands associated with the oxygen-containing complexes is greater for n-Ge single crystals. The value of $\Delta\delta/\Delta\Phi$ for the absorption band at 865 cm^{-1} in n-Si at the flows $\Omega \geq 1 \cdot 10^{17}$ el./cm^2 is many times smaller than for A-centers and VO_iP complexes. As noted above, this is explained by the relatively low concentration of interstitial carbon C_i, which after irradiation participates in the formation of C_iO_i complexes.

4. Conclusions

It was established that the main radiation defects responsible for the optical and photoelectric properties of electron-irradiated n-Ge and n-Si single crystals are VO_iI_{2Ge} complexes in germanium, A-centers, and VO_iP and C_iO_i complexes in silicon. Increasing the electron irradiation flow did not lead to the creation of new defects in n-Ge and n-Si, but only affected the intensity of the absorption bands associated with these radiation defects. Based on the analysis of the absorption spectra and the numerical estimates of the relative increase in the photosensitivity coefficients due to created radiation defects, it was established that the formation of A-centers and VO_iP complexes in the bulk of n-Si is more effective with an increase in the electron irradiation flow. Along with the intrinsic absorption bands of 1.1 and 1.8 µm in silicon and germanium, respectively, additional bands were identified in the long-wavelength region of the IR spectrum for electron-irradiated n-Ge and n-Si single crystals (12 µm absorption band for A-centres and VO_iP complexes in silicon, 15 µm for the VO_iI_2Ge complex in germanium and 11.6 µm for the C_iO_i complex in silicon); this fact will be of practical importance for the development of receivers for simultaneous monitiring of short- and long-wave IR radiation based on such irradiated germanium and silicon single crystals.

The obtained semiconductor “uncooled” materials of germanium and silicon, which were additionally exposed to radiation treatment, can become an alternative to the much more expensive materials of HgCdTe, PbSnTe and other narrow-gap semiconductors, which are used for the manufacture of infrared missile homing heads, thermal imagers, carbon dioxide sensors and require, as a rule, nitrogen or cryogenic cooling.

References

1. B. Nabet, Photodetectors: Materials, Devices and Applications, Woodhead publishing, (2023), 512.
2. G. Kropotov, V. Rogalin, I. Kaplunov, *Crystals*, **14**(9), 796 (2024).
3. J. K. Poon at al., *Advances in Optics and Photonics,* **16**(1), 1 (2024).
4. D. Benedikovic at al., *Nanophotonics*, **10**(3), 1059 (2021).
5. C. Xiang at al., *Applied Physics Letters*, **118**(22), 220501 (2021)
6. S. Y. Siew at al., *J.Lightwave Technology*, **39**(13), 4374 (2021).
7. S. Lee, Advanced material and device applications with germanium, IntechOpen, (2018), p. 550.
8. S. Mane, International *Journal of All Research Education and Scientific Methods*, **10**, 76 (2022).
9. P.I. Baranskii, A.E. Belyaev, G.P. Gaidar, Kinetic Effects in Multi-Valley Semiconductors, Naukova Dumka: Kyiv, (2019), p. 448.
10. H. Klym, A. Ingram, O. Shpotyuk, O. Hotra, A. Popov, *Radiation Measurements,* **90**, 117 (2016).
11. H. Klym, I. Karbovnyk, M. Guidi, O. Hotra, A. Popov, *Nanoscale research letters*, **11**, 132.1 (2016).
12. A. El-Raheem, H. Abd El Rahman, E. Shaaban, N. Hamed, M. M. Wakkad, *SSRN Electronic Journal*, 4022315 (2022).
13. H. Klym, A. Ingram, O. Shpotyuk, J. Filipecki, I. Hadzaman, *Physica Status Solidi* c, **4**, 715 (2007).

14. C. Chen, S. Min, Q. Guo, Z. Xia, D. Liu, F. Xia, *Nano Letters*, **21**, 8385 (2021).
15. J. Duran, Silicon-based infrared photodetectors for low-cost imaging applications, Thesis of Doctor of Philosophy in Electro-Optics, University of Dayton, Ohio, (2019), p. 177.
16. M. Wang at al., Advanced Optical Materials, 9, 2001546 (2021).
17. M.G. Bartmann at al., *Nanotechnology*, **33**, 245201 (2022).
18. L. Reid at al., IEEE 16th International Conference on Group IV Photonics (GFP), 1 (2019)
19. L. Reid at al., IEEE 17th International Conference on Group IV Photonics (GFP), 1 (2021).
20. N.P. Khuchua at al., *Nanotechnology Perceptions*, **10**, 91 (2014)
21. N. Khuchua at al., *Solid State Phenomena,* **242**, 374 (2016).
22. S. V.Luniov, M. V. Khvyshchun, V. T. Maslyuk, IEEE 11th International Scientific and Practical Conference on Electronics and Information Technologies (ELIT), 295 (2019).
23. S. V. Luniov, M. V. Khvyshchun, A. I. Tsyz, V. T. Maslyuk, IEEE 12th International Conference on Electronics and Information Technologies (ELIT), 18 (2021).
24. G. Korotcenkov, Introduction in IR detectors. In Handbook of II-VI Semiconductor-Based Sensors and Radiation Detectors: Volume 2, Photodetectors. Cham: Springer International Publishing, (2023), p. 3–22.
25. Y. U. Peter, M. Cardona, Fundamentals of semiconductors: physics and materials properties, Springer Science & Business Media, (2010), p. 639.
26. V.P. Markevich at al., *Applied Physics Letters,* **81**, 1821 (2002).
27. V.P. Markevich at al., *Physica B: Condensed Matter*, **340,** 844 (2003).
28. S.V. Luniov, A.I. Zimych, P.F. Nazarchuk, V.T. Maslyuk, I.G. Megela, *Nuclear Physics and AtomicEnergy*, **17**, 47 (2016).
29. S. V. Luniov, A.I. Zimych, P.F. Nazarchuk, V.T. Maslyuk, I.G. Megela, *Journal of Physical Studies*, **19**, 4704 (2015)
30. I.A. Kaplunov, V. E. Rogalin, *Photonics*, **13**, 88 (2019).
31. L.I. Murin, V.P. Markevich, T. Hallberg, J.L. Lindström, *Sol. St. Phenomena*, **69-70,** 309 (1999).
32. J.M. Trombetta, G.D. Watkins, *Appl. Phys. Lett.,* **51**, 1103 (1987).
33. M.I. Gritsenko, O.O.Kobzar, Yu.V Pomozov, M.G. Sosnin, L.I. Khirunenko, *Ukr. J. Phys.*. **55,** 222 (2010).
34. Sergiy Luniov, Andriy Zimych, Mykola Khvyshchun, Mykola Yevsiuk, Volodymyr Maslyuk, *Eastern-European Journal of Enterprise Technologie*s, **6**, 35 (2018).
35. S.V. Luniov, V.V. Lyshuk, V.T. Maslyuk, O. V. Burban, Latvia*n Journal of Physics and Technical Sciences*, **56**, 45 (2019).
36. A.V. Fedosov, S.V. Luniov, S.A. Fedosov, *Ukrainian Journal of Physics*, **56**, 69 (2011).