UDC 621.315.592.3

DOI 10.36910/775.24153966.2025.82.6

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КІНЕТИКА ВІДПАЛУ РАДІАЦІЙНИХ ДЕФЕКТІВ В ОПРОМІНЕНОМУ ЕЛЕКТРОНАМИ n-Ge

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Одержано кінетичні рівняння для опису ізотермічного відпалу опромінених електронами з енергією 10 MeB та потоком Ф=5·10¹⁵ ел./см² монокристалів германію, легованих домішкою сурми, концентрацією Nd=5·10¹⁴ см⁻³. На основі одержаних експериментальних результатів температурної залежності коефіцієнта Холла та обчислених значень концентрації утворених при опромінені та відпалі комплексів VO_iI_{2Ge} в монокристалах германію визначено енергію активації відпалу для даних комплексів та областей розвпорядкування. З одержаних результатів слідує, що ядра областей розвпорядкування є менш термічно стійкими, ніж комплекси VO_iI_{2Ge}.

Ключові слова: монокристали германію, електронне опромінення, ізотермічний відпал, кінетика відпалу, енергія активації відпалу.

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KINETICS OF ANNEALING OF RADIATION DEFECTS IN ELECTRON-IRRADIATED n-Ge

The kinetic equations for describing the isothermal annealing of germanium single crystals, doped by the antimony impurity with the concentration of N_d =5· 10^{14} cm⁻³, irradiated by the electrons with the energy of 10 MeV and a flow of Ω =5· 10^{15} el/cm², were obtained. The annealing activation energy for complexes and disordered regions based on the experimental results of the temperature dependence of the Hall coefficient and the calculated concentration values of the VO_iI_{2Ge} complexes, created during irradiation and annealing in germanium single crystals, was determined. The results show that the cores of the disordered regions are less thermally stable than the VO_iI_{2Ge} complexes.

Keywords: germanium single crystals, electron irradiation, isothermal annealing, annealing kinetics, annealing activation energy.

Statement of the problem. Penetrating radiation makes it possible to control the electrical parameters of semiconductor materials and optimize the production technology of semiconductor devices and microcircuits made on their basis [1-4]. This is due to the growing demand for semiconductor integrated circuits, the complexity of semiconductor technologies, and the reduction in the geometric dimensions of the active regions of semiconductor structures. In addition, due to the rapid development of space technology, there is considerable interest in studying the radiation-stimulated degradation of semiconductors and integrated circuits and determining the levels of radiation resistance of the element base of spacecraft electronics [5-8]. The performance of spacecraft equipment is affected by the ionizing radiation of outer space (high-energy electrons, protons, heavy element ions). The effect of radiation on the elements of the spacecraft's on board equipment leads to their failure due to degradation processes in semiconductors, which is associated with the accumulation of the absorbed dose and radiation effects [9-13].

To reduce the concentration of radiation defects and ensure the stability of the electrical parameters of semiconductors, special thermal annealing is performed, which leads to the formation of other types of thermally stable and, accordingly, time-stable defects [14-16]. In work [14], the creation and annealing of defects in germanium irradiated by different proton flows with the energy of 15 MeV at 300 K by positron annihilation spectroscopy are investigated. Two characteristic temperature stages of isochoric annealing were identified. The first stage from 400 to 500 K is associated with the annealing of vacancy complexes. At 420 K, vacancy clusters consisting of two vacancies began to appear. Further, an increase in the annealing temperature to 520 K leads to forming clusters of approximately three vacancies. The second stage of annealing occurs in the temperature range of 550–650 K, which is associated with the annealing of vacancy clusters. To describe the results of positron lifetime measurements, a model of negative-type positron traps was used. According to this model, these defects anneal in the temperature range of 500-600 K. The determined average lifetime of positrons after annealing at 740 K was almost the same as that for unirradiated germanium. In [15], studies of the annealing of proton-irradiated germanium in the temperature range of 35–300 K reveal two stages. The first at 100 K is associated with the annealing of Frenkel pairs, and the second at 200 K is associated with the annealing of monovacancies. At annealing temperatures above 200 K, mobile neutral monovacancies merged into divacancies. In [16], it was found that in fluorineimplanted germanium, fluorine enriches the germanium matrix with various vacancy-like clusters, the structure of which depends on the annealing temperature. It was found that low concentrations of fluorine saturate the Ge matrix with high concentrations of divacancy complexes, which are effectively annealed. High concentrations of fluorine stabilize monovacancy-like complexes, which are thermally stable even after high-temperature annealing. When conducting such studies, it is important to have information about the annealing activation energy and the frequency of jumps of radiation defects to the drain. The use of these parameters will allow estimating the time of stable operation of electronic equipment of spacecraft, atomic and nuclear power, which may contain elements made based on irradiated and additionally heat-treated material. At the same time, the construction of mathematical models of radiation defect annealing will provide scientific and methodological recommendations to engineers and scientists working in the field of radiation technologies of semiconductors, regarding the creation of radiation-resistant semiconductor devices and sensors with predetermined properties.

Setting tasks. Obtaining kinetic equations for isothermal annealing of radiation defects in n-Ge single crystals, irradiated by the electrons with the energy of 10 MeV and determining the annealing activation energy for the created defects.

Presentation of the main material. We developed a mathematical model of isothermal annealing kinetics for single crystals of germanium, doped by the antimony, with the concentration of N_d=5·10¹⁴ cm⁻¹ ³, irradiated by the electrons with the energy of 10 MeV and a flow of Ω =5·10¹⁵ el./cm². In work [17], studies of isothermal annealing processes were carried out for the same electron-irradiated n-Ge single crystals. It was established based on measurements of the Hall effect and solutions of the electroneutrality equation that under given conditions of electron irradiation, both simple defects (VO_iI_{2Ge} complexes) and complex defects (disorder regions) are formed in germanium single crystals. Moreover, the energy spectrum of radiation defects for n-Ge samples did not change after annealing. From the analysis of the temperature dependence of the Hall coefficient and the calculated values of the concentration of VO_iI_{2Ge} complexes formed during irradiation and annealing in germanium single crystals, it was concluded that the processes of both annealing and generation of VO_iI_{2Ge} complexes co-occur. The generation of these complexes is associated with the annealing of disordered regions, which have lower annealing activation energy. Therefore, the different mutual contributions of the annealing processes and the generation of the formed radiation defects explain the normal and anomalous annealing obtained in this work. Calculations of the annealing activation energy and frequency factor for VO_iI_{2Ge} complexes and disordered regions, the results of measurements of the temperature dependences of the Hall constant for such n-Ge single crystals after annealing at T₁=433 K and T₂=448 K and the concentration values of VO_iI_{2Ge} complexes for given annealing temperatures were used. The dependences of the concentration of VO_iI_{2Ge} complexes on the isothermal annealing time are presented in Fig. 1.

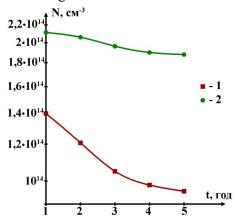


Fig. 1. Dependencies of the concentration of VO_iI_{2Ge} complexes on the time of isothermal annealing for n-Ge single crystals, irradiated by the electrons with an energy of 10 MeV and a flow of Ω =5·10¹⁵ el./cm² at different isothermal annealing temperatures T, K: 1 –448, 2 –433.

The nonlinear nature of the dependences of the concentration of these complexes on the annealing time, obtained on a semi-logarithmic scale, indicates that the annealing kinetics of the formed defects cannot be described by an exponential law, which is characteristic only for the annealing of defects of the same type:

$$N = N_0 e^{-\frac{t}{\tau}},\tag{1}$$

where N – is the defect concentration after annealing, N_0 – is the defect concentration before annealing, t – is the annealing time, τ – is the average defect lifetime.

For the case of parallel annealing processes of VO_iI_{2Ge} complexes and nuclei of disordered regions in the studied n-Ge single crystals, the following system of equations can be written:

$$\begin{cases}
\frac{dN_{A}}{dt} = \frac{N_{V}}{\tau_{1}} - \frac{N_{A}}{\tau_{2}}, \\
\frac{dN_{V}}{dt} = \frac{N_{V}}{\tau_{1}} + \frac{N_{A}}{\tau_{2}}.
\end{cases} (2)$$

where N_A , N_V – concentrations of VO_iI_{2Ge} complexes and vacancies at an arbitrary point in time, τ_1 , and τ_2 are the average lifetimes of the vacancy and VO_iI_{2Ge} complex, respectively.

From the solution of system (2) we obtain that

$$N_{A}(t) = -\frac{N_{0}(k_{2}\tau_{1} + \frac{\tau_{1}}{\tau_{2}})}{\tau_{1}(k_{1} - k_{2})} e^{k_{1}t} + \frac{N_{0}(k_{1}\tau_{1} + \frac{\tau_{1}}{\tau_{2}})}{\tau_{1}(k_{1} - k_{2})} e^{k_{2}t},$$

$$(3)$$
where $k_{1} = \frac{-\left(\frac{\tau_{1}}{\tau_{2}} - 1\right) + \sqrt{\left(\frac{\tau_{1}}{\tau_{2}} - 1\right)^{2} + \frac{8\tau_{1}}{\tau_{2}}}}{2\tau_{1}}, \quad k_{2} = \frac{-\left(\frac{\tau_{1}}{\tau_{2}} - 1\right) - \sqrt{\left(\frac{\tau_{1}}{\tau_{2}} - 1\right)^{2} + \frac{8\tau_{1}}{\tau_{2}}}}{2\tau_{1}}.$

To find the times τ_1 and τ_2 , we write equation (3) for two different isothermal annealing times t_1 and t_2 . As a result, we obtain a system of equations:

$$\begin{cases}
N_{A}(t_{1}) = -\frac{N_{0}(k_{2}\tau_{1} + \frac{\tau_{1}}{\tau_{2}})}{\tau_{1}(k_{1} - k_{2})} e^{k_{1}t_{1}} + \frac{N_{0}(k_{1}\tau_{1} + \frac{\tau_{1}}{\tau_{2}})}{\tau_{1}(k_{1} - k_{2})} e^{k_{2}t_{1}}, \\
N_{A}(t_{2}) = -\frac{N_{0}(k_{2}\tau_{1} + \frac{\tau_{1}}{\tau_{2}})}{\tau_{1}(k_{1} - k_{2})} e^{k_{1}t_{2}} + \frac{N_{0}(k_{1}\tau_{1} + \frac{\tau_{1}}{\tau_{2}})}{\tau_{1}(k_{1} - k_{2})} e^{k_{2}t_{2}}.
\end{cases} (4)$$

To perform such calculations, the experimental results of annealing at temperatures T_1 =433 K and T_2 =448 K were used, fig. 1. To find the activation energy of annealing of the formed radiation defects, we write down the expressions for the average lifetime of the VO_iI_{2Ge} complex and vacancies at two different annealing temperatures T_1 and T_2 [18]:

$$\tau_1(T_1) = \frac{1}{V_1} e^{\frac{E_{a1}}{kT_1}}, \ \tau_1(T_2) = \frac{1}{V_1} e^{\frac{E_{a1}}{kT_2}}, \tag{5}$$

$$\tau_2(T_1) = \frac{1}{v_2} e^{\frac{E_{a2}}{kT_1}}, \ \tau_2(T_2) = \frac{1}{v_1} e^{\frac{E_{a2}}{kT_2}}. \tag{6}$$

From the solutions of equations (5) and (6), we obtain that $E_{a1} = 0.92 \,\mathrm{eV}$ is the activation energy of the annealing of the disordered region and $E_{a2} = 1.04 \,\mathrm{eV}$ is the activation energy of the annealing of the VO_iI_{2Ge} complex, $v_1 = 2.52 \cdot 10^6 \,\mathrm{s}^{-1}$ and $v_2 = 1.07 \cdot 10^8 \,\mathrm{s}^{-1}$ are the frequency factors for the vacancy and the VO_iI_{2Ge} complex, respectively.

Conclusions. The proposed theoretical model of annealing, considering the found activation energies of annealing and frequency factors for these defects, well describes the annealing kinetics, which was experimentally revealed in [17]. According to the data of [19], the annealing of VO_i complexes in germanium after γ -irradiation occurred in the temperature range of 383-403 K. The obtained values of the activation energy of annealing for this defect and the frequency factor turned out to be equal to 0,94 eV and $4\cdot10^7$ s⁻¹, respectively. In our case, the activation energy of annealing of the VO_iI_{2Ge} complex is equal to 1,04 eV, which indicates its greater thermal stability. The obtained kinetic equations of isothermal annealing and its found parameters allow us to predict the stability over time of operation of electronic elements made based on germanium, which is additionally subjected to radiation and heat treatment.

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