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FEATURES OF RADIATION-DEFECT ANNEALING IN n-Ge SINGLE CRYSTALS IRRADIATED WITH HIGH-ENERGY ELECTRONS

The isothermal annealing of n-Ge single crystals irradiated with 10-MeV electrons to the fluence $\Phi = 5\times10^{15}$ cm^{-2} has been studied. On the basis of the measured temperature dependences of the Hall constant and by solving the electroneutrality equations, the concentrations of radiation-induced defects (A-centers) in irradiated n-Ge single crystals are calculated both before and after the annealing. An anomalous increase of the Hall constant is found, when the irradiated n-Ge single crystals were annealed at $T_{\rm an} = 403$ K for up to 3 h. The annealing at the temperature $T_{\rm an} = 393$ K for 1 h gave rise to the np *conversion in the researched crystals. The revealed effects can be explained by the concentration growth of A-centers owing to the generation of vacancies at the annealing of disordered crystal regions.*

Keywords: isothermal annealing, radiation-induced defects, disordered regions, np conversion, germanium single crystals.

1. Introduction

Radiation technologies are a powerful tool to purposefully change the properties of solids and, accordingly, to create various complex devices of functional electronics on their basis [1–4]. Under the irradiation action, various defects are generated in solids and significantly modify their mechanical, electrical, optical, and other physical properties. Semiconductor materials (the basic ones are Ge and Si) are especially sensitive to the presence of radiation-induced effects. Those materials, being modified by dopants or radiation-induced defects, are raw materials for the creation of elements of a modern electronic equipment [5,6]. Furthermore, germanium and silicon are used in CMOS technologies for fabricating the electronic devices [7, 8] and in nanostructures (Ge quantum dots and Si/Ge heterostructures) [9, 10], which can also be subjected to the action of external radiation fields, for example, when the electronic equipment is exploited in spacecrafts [11].

The electrophysical properties of irradiated Ge and Si single crystals are mainly determined by the presence of secondary radiation-induced defects of various kinds, which arise due to quasichemical reactions among vacancies, interstitial atoms, and chemical impurity atoms [1–3]. As a rule, such defects create deep energy levels in the forbidden band of germanium and silicon [12]. At present, the microstructure and energy spectra of radiation-induced defects in Si are studied much more than those in Ge, which is mainly associated with a limited applicability of EPR to the latter material [13, 14]. For instance, the vacancy-oxygen complex (the A-center) is one of the most studied defects in Si single crystals. The identification of this defect in Ge is a more complicated

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task [15]. In particular, according to the results of spectroscopic researches in works [16, 17], a spread of the absorption band at 620 cm^{-1}, which is associated with the A-center, and its dependence on the annealing temperature (from 50 to 150 °C) were observed. As a result, the control over the A-center using this band becomes ambiguous. Moreover, this band might be attributed to only one of the charge states of this complex.

The measurement of the Hall effect in combination with the heat treatment (annealing) is an effective method for studying the parameters of radiation-induced defects in Ge single crystals. As is known, the annealing is used to restore the electrophysical properties of irradiated semiconductors. The ultimate purpose of the annealing is (i) to determine the annealing activation energy and the frequency of jumps of defects onto a sink and (ii) to establish whether a reaction giving rise to the formation of new, more thermostable defects is possible [18]. In addition, the annealing processes may possess an application value, because, by properly selecting the optimum temperature and annealing time, it is possible to purposefully control the defect concentration and thereby to enhance the thermal, magnetic, tenso-, and photosensitivity of a semiconductor material. On the basis of such materials, various sensors and electronic devices can be created. The data obtained for the annealing activation energy and the jump frequency of radiation-induced defects onto the sink also allow one to estimate the time of stable operation of an electronic equipment containing elements based on the irradiated material. Therefore, it is of interest, from the theoretical and practical viewpoints, to study both the processes taking place at the annealing of radiation-induced defects in Ge single crystals and the influence of those defects on various physical properties of Ge.

2. Experimental Results and Theoretical Calculations

In our previous work [19], the Hall effect was measured in n-Ge single crystals doped with the antimony admixture to the concentration $N_d = 5 \times 10^{14}$ cm^{-3} and irradiated with 10-MeV electrons to various fluences Φ. At the electron irradiation fluence $\Phi = 5 \times 10^{15}$ cm^{-2}, radiation-induced defects with the deep energy level $E_C - 0.27$ eV, which belongs to the A-center [13, 20], were effectively generated. In work [13], a point-like defect in Ge with a similar energy spectrum was simulated as a complex consisting of a vacancy, an oxygen atom, and two interstitial germanium atoms (VOI_{2Ge}). Irradiated n-Ge specimens had the conductivity of the n-type, and the np conversion was observed only at high irradiation doses. In work [21], we carried out a comparative analysis of the experimental and theoretical temperature dependences of the Hall mobility obtained for the same n-Ge single crystals. It allowed us to establish that, under the irradiation conditions mentioned above, besides A-centers, disordered regions are generated as well.

The majority of publications dealing with the annealing of radiation-induced defects in germanium were devoted to the study of the annealing of simple radiation defects (A- and E-centers, divacancies, and other defects), which dominate at electron irradiation energies lower than 10 MeV, or complex defects (disordered regions), which emerge in Ge single crystals irradiated with electrons with energies of a few dozens of MeVs [22]. In those researches, the electrophysical properties of germanium single crystals after the annealing were supposed to be mainly governed by the mechanisms of annealing of defects belonging to a definite single type. The case of simultaneous annealing of both simple and complex defects has been little studied. As a result, there are no adequate models that would explain the mechanisms of such annealing, so that its influence on the physical properties of germanium single crystals remains obscured.

Therefore, in this work, we focused our attention on the isothermal annealing of n-Ge single crystals irradiated with 10-MeV electrons to the fluence $\Phi = 5 \times 10^{15}$ cm^{-2}. The experimental single crystalline n-Ge specimens had characteristic dimensions of $1 \times 2 \times 10$ mm^3. They were irradiated on an electron accelerator (microtron) M-30, whose parameters allowed us to form a uniform radiation field with a density of 4×10^{11} electron/(cm^2s) over an area of 100 cm^2. The specimens were cooled down by means of nitrogen vapor. The temperature of irradiated specimens was monitored remotely with the help of a copper-constantan thermocouple. The parameters of the latter were found to be resistant to a prolonged radiation exposure. The role of bremsstrahlung γ- and neutron radiation in the defect formation in n-Ge was insignificant under the given experimental conditions, because the corresponding contribution to the radiation field of M-30 did not exceed 1%. The probability of photo- or neutron-nuclear reactions at an electron energy of 10 MeV is 10^4 to 10^5 times lower than the probability of formation of radiation-induced defect: the cross-section of the γ-n reaction is about 10 mb, and that of defect formation equals 10–100 b. Therefore, the processes of defect formation in the examined n-Ge single crystals were associated with the high-energy electron irradiation only.

Figure 1 demonstrates the measurement results for the temperature dependences of the Hall constant for specimens annealed for one hour. As one can see, at the annealing temperatures $T_B = 433$ and 448 K, the Hall constant diminishes in comparison with that in irradiated (but not annealed) specimens within the whole examined temperature interval. This fact testifies to a growth of the electron concentration in the conduction band owing to the annealing of A-centers. The prolongation of the annealing time also resulted in a further reduction of the Hall constant and, accordingly, the concentration of A-centers. After the annealing at the temperature $T_B = 403$ K for 1 h, an anomalous growth of the Hall constant with respect to irradiated (but not annealed) specimens was revealed (Fig. 1, curve *3*), which lasted up to 3 h (Fig. 2, curve *2*).

The annealing of the n-Ge specimen at the temperature $T_B = 393$ K for an hour stimulated its conversion into the p-type specimen. A further thermal treatment for 1 to 3 h at the indicated annealing temperature (Fig. 3, curves *1* and *2*) led to a decrease of the Hall constant at $T > 210$ K, which testifies to an increase of the hole concentration in the valence band of annealed germanium specimens. After the 6-h annealing, Ge restored the n-type conductivity owing to a reduction of the concentration of A-centers. The further annealing led to a reduction of the Hall constant.

A change of the Hall constant R_H after the annealing of irradiated n-Ge single crystals can be induced by both the variation in the concentration of electrically active defects (A-centers) and the appearance of new complexes with a different energy spectrum [1, 23]. Therefore, in order to interpret the results obtained, we calculated the concentration and the energy spectrum of radiation-induced defects in the annealed germanium specimens.

Let the equilibrium concentration of radiation defects be equal to N in an n-germanium specimen after

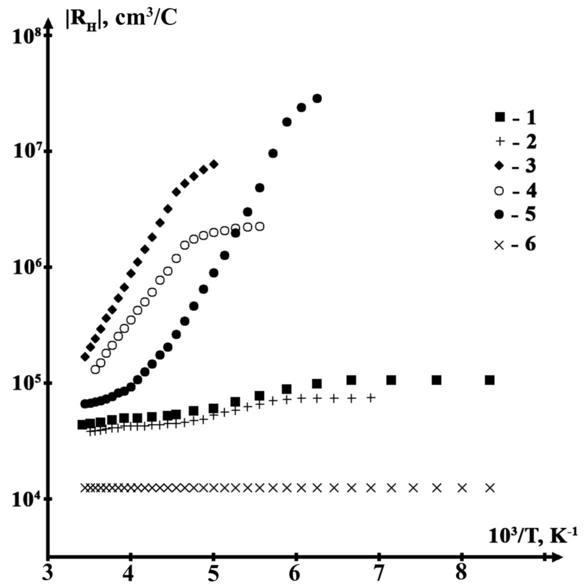

Fig. 1. Temperature dependences of the Hall constant, $|R_H| = f(10^3/T)$, for irradiated n-Ge single crystals after their isothermal annealing for 1 h at various temperatures $T_B = 433$ (*1*), 448 (*2*), 403 (*3*), and 393 K (*4*). Curve *5* corresponds to an unannealed specimen, and curve *6* to non-irradiated one

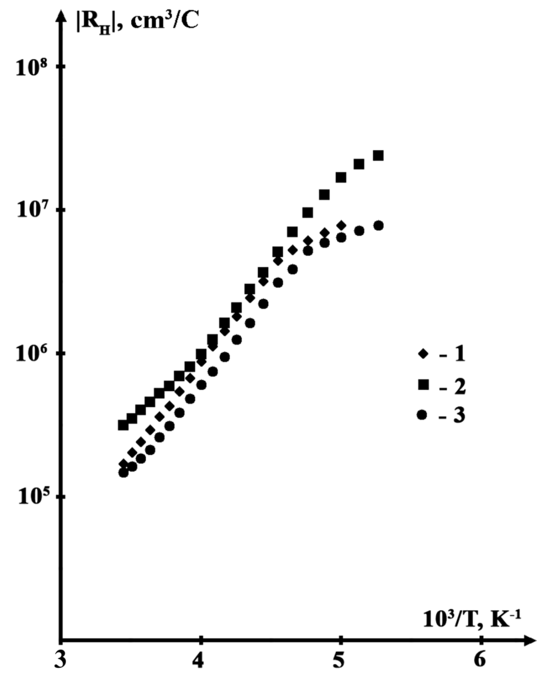

Fig. 2. Temperature dependences of the Hall constant, $|R_H| = f(10^3/T)$, for irradiated n-Ge single crystals at the isothermal annealing temperature $T_B = 403$ K and various annealing times $t = 1$ (*1*), 3 (*2*), and 5 h (*3*)

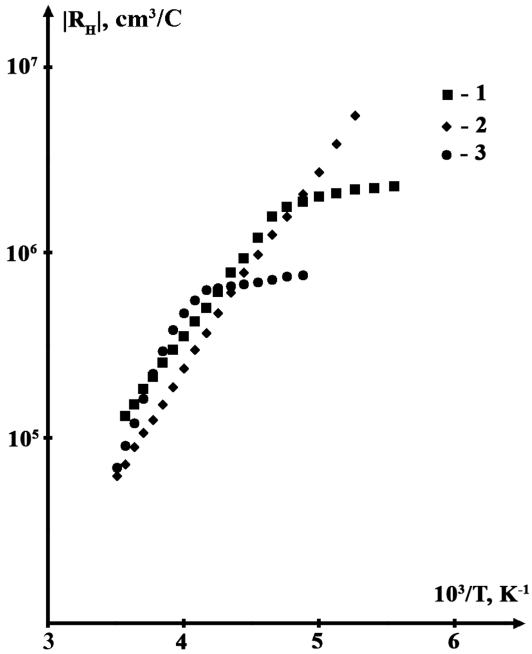

Fig. 3. Temperature dependences of the Hall constant, $|R_{\rm H}| = f(10^3/T)$, for irradiated n-Ge single crystals after the isothermal annealing at the temperature $T_{\rm B} = 393$ K and various annealing times $t = 1$ (*1*), 3 (*2*), and 6 h (*3*)

the annealing, and let L acceptor levels correspond to every such defect. Then, at temperatures, when shallow donors are completely ionized, and the upper energy level of radiation-induced defects is partially ionized, the following electroneutrality equation can be written down:

$$N\,(L-1) + n_a + n = N_d. \tag{1}$$

Here, n_a is the electron concentration at the acceptor level with the highest energy, n the concentration of electrons in the conduction band, and N_d the donor impurity concentration. In view of the expressions for the concentrations n_a and n [24],

$$n_a = \frac{N}{2\exp\left(\frac{E_a-F}{kT}\right)+1}, \quad n = N_c \exp\left(\frac{F}{kT}\right). \tag{2}$$

Equation (1) can be rewritten in the form

$$N\,(L-1) + \frac{N}{1+\frac{2N_c}{n}\exp\left(\frac{E_a}{kT}\right)} + n = N_d, \tag{3}$$

where $N_{\rm c} = \frac{(2m_n kT)^{3/2}}{4\pi^3\hbar^3}$ is the effective density of states in the conduction band, and F the Fermi energy. Equation (3) includes three unknown parameters of radiation-induced defects, which could change in comparison with irradiated (but not annealed) specimens. These are the concentration N of radiation-induced defects, the number L of acceptor levels belonging to every such defect, and the ionization energy E_a of the acceptor level with the highest energy. In order to calculate those parameters, let us write Eq. (3) for three different electron concentrations at three different temperatures. As a result, we obtain the following system of equations:

$$\begin{cases} N\,(L-1) + \dfrac{N}{1+\frac{2N_c(T_1)}{n_1}\exp\left(\frac{E_a}{kT_1}\right)} + n_1 = N_d, \\ N\,(L-1) + \dfrac{N}{1+\frac{2N_c(T_2)}{n_2}\exp\left(\frac{E_a}{kT_2}\right)} + n_2 = N_d, \\ N\,(L-1) + \dfrac{N}{1+\frac{2N_c(T_3)}{n_3}\exp\left(\frac{E_a}{kT_3}\right)} + n_3 = N_d. \end{cases} \tag{4}$$

The change of the conductivity type (the np conversion) in a semiconductor doped with donor impurities takes place owing to the strong compensation of shallow donor energy levels by acceptor levels of radiation-induced defects. Suppose that (i) there are several acceptor levels in a semiconductor with the p-type conductivity, (ii) the acceptor level with the lowest energy is partially filled with electrons, and (iii) all others levels are completely empty. Then, for the p-specimens annealed at $T_{\rm B} = 393$ K, we may write

$$N_d + p = n_a, \tag{5}$$

$$p = N_V \exp\left(\frac{-E_g - F}{kT}\right), \tag{6}$$

where p is the concentration of holes in the valence band, E_g the band gap width in germanium, $N_V = \frac{(2m_p kT)^{3/2}}{4\pi^3\hbar^3}$ is the effective density of states in the valence band, and $m_p = 0.3m_0$ is the effective mass of the density of states for holes. Taking expression (6) into account, we obtain

$$N_d + p = \frac{N}{1+2\frac{p\exp\left(\frac{E_g}{kT}\right)}{N_V}\exp\left(\frac{E_a}{kT}\right)}. \tag{7}$$

Now, in order to determine the concentration of radiation-induced defects and the ionization energy

E_a of the acceptor level, let us write Eq. (7) for the hole concentrations p_1 and p_2 at the temperatures T_1 and T_2, respectively:

$$\begin{cases} N_d + p_1 = \dfrac{N}{1 + 2\frac{p_1 \exp\left(\frac{E_g}{kT_1}\right)}{N_V(T_1)} \exp\left(\frac{E_a}{kT_1}\right)}, \\ N_d + p_2 = \dfrac{N}{1 + 2\frac{p_2 \exp\left(\frac{E_g}{kT_2}\right)}{N_V(T_2)} \exp\left(\frac{E_a}{kT_2}\right)}. \end{cases} \tag{8}$$

Based on the values of the effective mass of the density of states for electrons in the conduction band and holes in the valence band of germanium, the concentration of antimony impurity $N_d = 5\times10^{14}$ cm^{-3}, and the experimental values of electron and hole concentrations that were determined from the temperature dependences of the Hall constant, we calculated the above-indicated unknown parameters for radiation-induced defects in Ge specimens subjected to the annealing in various regimes. The results of calculations showed that the energy spectrum of radiation defects in the annealed specimens turned out similar to that determined by us earlier in work [19] for irradiated (and not annealed) n-Ge single crystals. In particular, the deep level of A-center at $(E_c - 0.27)$ eV dominated in germanium with the n-type conductivity, and the level at $(E_V + 0.27)$ eV in germanium with the p-type conductivity. This fact testifies that the formation of defects of other types at the annealing is either impossible or has a low efficiency. The calculation results for the concentration of A-centers in annealed specimens are quoted in Table.

Concentration of A-centers in irradiated Ge single crystals after the isothermal annealing

Annealing temperature T_{B}, K	Annealing time t, h	Concentration of A-centers N, cm^{-3}
448	1	1.4×10^{14}
433	1	2.1×10^{14}
	1	4.5×10^{14}
403	3	4.6×10^{14}
	5	4.4×10^{14}
	1	5.4×10^{14}
393	3	6.2×10^{14}
	6	3.8×10^{14}
Unannealed specimen	–	2.8×10^{14}

A high concentration of vacancies in the kernel of a disordered region is known to facilitate its reconstruction and the diffusion of vacancies into the conducting crystal matrix [22]. Therefore, the diffusing vacancies can enter again into quasichemical reactions with oxygen and interstitial germanium atoms to produce new A-centers. This scenario can explain the anomalous annealing obtained by us at the temperatures $T_{\mathrm{B}} = 403$ and 393 K. Longer annealing times lead to a reduction in the concentration of disordered regions and, accordingly, the concentration of vacancies, from which new A-centers can be formed. As a result of such long-term annealing, new disordered regions, which are thermally more stable, can also be formed [22]. Then the concentration of vacancies that arose at the annealing of the kernels of disordered regions will decrease. These processes are responsible for that the processes of A-center annealing begin to prevail over the processes of A-center generation at the annealing temperatures $T_{\mathrm{B}} = 403$ K (for more than 3 h) and 393 K (for more than 6 h). In turn, this stimulates a reduction of the Hall constant in the case where $T_{\mathrm{B}} = 403$ K, and the annealing time equals 5 h (Fig. 2, curve *3*), as well as the inverse *pn* conversion in irradiated germanium within 6 h in the case of the annealing temperature $T_{\mathrm{B}} = 393$ K.

3. Conclusions

From the analysis of the obtained experimental results and the results of theoretical calculations, it follows that, for the researched n-Ge single crystals irradiated with high-energy (10 MeV) electrons, the kinetics of accumulation and annealing of radiation-induced defects can be explained by two mechanisms: 1) annealing of simple (point-like) defects belonging to A-centers and 2) generation of A-centers owing to the annealing of the kernels of disordered regions, for which the annealing activation energy is lower than that for A-centers. The efficiency of those mechanisms depends on both the temperature and the isothermal annealing time. This fact can explain the anomalous growth of the Hall constant at the annealing temperature $T_{\mathrm{B}} = 403$ K during 3 h and the change of the conductivity type (the np conversion) in irradiated germanium single crystals after their annealing at the temperature $T_{\mathrm{B}} = 393$ K.

The isothermal annealing research of n-Ge single crystals irradiated with high-energy electrons also has an application value. The controllable change of the concentration of radiation defects with deep energy levels by the annealing should enhance the thermal, photo-, tenso-, and magnetic sensitivities of irradiated germanium. The latter can be used as a basis for the creation of high-sensitive temperature, magnetic, and pressure sensors, as well as elements of the infrared technique.

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ОСОБЛИВОСТІ ВІДПАЛУ
РАДІАЦІЙНИХ ДЕФЕКТІВ В МОНОКРИСТАЛАХ n-Ge,
ОПРОМІНЕНИХ ЕЛЕКТРОНАМИ ВИСОКИХ ЕНЕРГІЙ

Р е з ю м е

Досліджено ізотермічний відпал опромінених потоком електронів $\Phi = 5 \cdot 10^{15}$ см$^{-2}$ з енергією 10 МеВ монокристалів n-Ge. На основі одержаних температурних залежностей сталої Холла, з розв'язків рівнянь електронейтральності, було обчислено концентрацію радіаційних дефектів, що належать А-центрам, в опромінених монокристалах n-Ge до і після відпалу. При температурі відпалу $T_{\rm B} = 403$ K, для часів відпалу до трьох годин, було виявлено аномальне збільшення сталої Холла. Відпал при температурі $T_{\rm B} = 393$ K протягом однієї години призвів до n–p конверсії. Дані ефекти пояснюються зростанням концентрації А-центрів за рахунок генерації вакансій, які утворюються при відпалі ядер областей розвпорядкування.