THE ANNEALING OF DEFECT CLUSTERS IN CZOCHRALSKI-GROWN Si AND Si⟨Ge⟩ SAMPLES

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Czochralski-grown n-type silicon (Cz-Si) samples doped by germanium ($N_{\mathrm{Ge}} = 2 \times 10^{20}$ cm^{-3}) and without that were investigated after the irradiation by fast neutrons. The isothermal annealing of n-Si⟨Ge⟩ after the irradiation with a fluence of 1.4×10^{14} neutr./cm^2 was studied for three temperatures. It is shown that the annealing of defect clusters is caused by the annihilation of vacancy-type defects in the clusters with interstitial defects. The annealing of neutron-irradiated n-type Cz-Si by gamma irradiation was observed.

1. Introduction

It is known that the electrophysical properties of semiconductors are very susceptible to any damages of the crystal lattice. Under the nuclear irradiation, both point defects and more complex lattice damages, for example in the form of defect clusters, are created in crystals [1]. So, when the energy of incoming particles is only slightly more than the threshold energy which is required to displace an atom from a lattice site, mainly the simple point defects are formed, namely, Frenkel pairs, space-separated vacancies, and interstitial atoms. In the case where the particle energy exceeds the energy required for an initially shifted atom to create the entire cascade of displaced atoms, the disordered regions surrounded by the space-charge region are formed in the crystal lattice. Such regions are named as defect clusters.

The formation of such disordered regions considerably influences the lifetime, mobility, and effective concentration of carriers in the irradiated crystals. The properties of a semiconductor with defect clusters qualitatively differ from those of the materials where simple defects are uniformly distributed. The crystals, in which the linear sizes of disordered regions have order of magnitude near several hundreds of interatomic distances, are, in fact, the two-phase system: the conducting matrix—cluster defects.

For a deeper insight into the nature of cluster defects and their influence on the parameters of semiconductor devices, the study of annealing processes, which are related to the transformation of defect clusters and the annihilation of excess defects, has the important significance. The investigation of the annealing processes also gives possibility to obtain the values of the activation energy of defects and values of the parameters which determine the kinetics of various reactions between defects of the crystal lattice [2].

The investigations of the annealing of defect clusters formed under the irradiation by fast-pile neutrons in the crystals of silicon and silicon with the germanium dopant and the changes of the volume fraction occupied by defect clusters in the preliminarily neutron-irradiated Cz-Si samples during their radiation annealing by (γ-quanta from ^{60}Co) are the main objectives of the presented work.

2. Experiment

Czochralski-grown n-type silicon samples (n-Si⟨Ge⟩) doped by germanium ($N_{(\mathrm{Ge})} \approx 2 \times 10^{20}$ cm^{-3}) with resistivity $\rho \sim 10$ Ωcm and with the carrier concentration before irradiation $n_0 \approx 5.15 \times 10^{14}$ cm^{-3}, as well as standard Cz-Si n-type samples without germanium impurity ($n_0 \approx 5.02 \times 10^{13}$ cm^{-3}) have been studied. The samples had the same concentration of oxygen $N_{(\mathrm{O}_i)} \approx (5\div6.4) \times 10^{17}$ cm^{-3}. The carbon concentration ($N_{(\mathrm{C})} \approx 1 \times 10^{17}$ cm^{-3}) was twice more in Si⟨Ge⟩ than that in Cz-Si. The concentrations of germanium, oxygen, and carbon were measured at room temperature, by using a Fourier-transform infrared spectrometer.

The irradiation was performed in the horizontal channel of a water-water reactor (WWR-M) with fluences of 1.4×10^{14} and 2×10^{13} neutr./cm^2 at room temperature. The flux of fast neutrons (I_f) was determined by a ^{32}S threshold detector (the threshold energy is $E = 0.95$ MeV) with an accuracy of 10 % and led to the energy of neutrons starting from ~100 keV. The ratios of the fluxes with various threshold energies I_f (0.1) / I_f (0.95) = 0.986/0.690) in the spectrum of fission neutrons were taken into account. Contacts were created by rubbing Al into the polished surface of Si.

The consecutive isothermal annealing of Si⟨Ge⟩ originally irradiated with a fluence of 1.4×10^{14} neutr./cm^2 was studied at three temperatures (20, 80, and 106 °C). The measurements were carried out in 2, 26, and 55 days at room temperature. At 80 and 106 °C, the time intervals of the annealing were 20, 100, and 300 min.

The radiation annealing of n-type Cz-Si samples, which were preliminarily irradiated at room temperature with a fluence of 2×10^{13} neutr./cm^2 of fast neutrons, was investigated with the use of the ^{60}Co gamma-irradiation.

3. Main Equations and Definitions

On the irradiation of the semiconductor by fast-pile neutrons to determine a change of the effective carrier concentration ($n_{\rm eff}$), the carrier removal rate from the conduction band not only by point defects but also by defect clusters is usually considered [3]:

$$\upsilon_e = \upsilon_{\rm p}(1-f) - n_0 \frac{f}{\Phi}. \quad (1)$$

Here, $\upsilon_{\rm p}$ is the carrier removal rate by point defects; $\upsilon_{\rm cl} = -n_0\ f/\Phi$ is the carrier removal rate by defect clusters; n_0 is the carrier concentration before irradiation; $f(T,\Phi) = 1 - \exp(-\Sigma V(T)\Phi)$ is the volume fraction occupied by defect clusters at temperature T after the irradiation by fast neutrons with a fluence Φ [4]; $V(T)$ is the average volume of a cluster [5]; and $\Sigma = 0.15$ cm^{-1} is the macroscopic cross-section of the defect cluster introduction [3]. Then the concentration of carriers ($n_{\rm cl}$) removed by defect clusters from the conduction band is proportional to the volume fraction occupied by clusters ($f(T,\Phi)$): $n_{\rm cl}(T,\Phi) = \upsilon_{\rm cl}\Phi = n_0 f(T,\Phi)$.

The $n_{\rm eff}$ can be determined as $n_{\rm eff} = n_0 + \upsilon_e$. However, we cannot use this formula, since the carrier removal rate by defects depends on Φ. The analysis of Eq. (1) shows that, with increase in the fluence, the carrier removal rate (υ_e) decreases at the expense of an increase of the volume fraction occupied by defect clusters. On the other hand, fast neutrons introduce the defects with deep levels, such as divacancies (V_2) and trivacancies (V_3), in the conducting matrix. Therefore, with increase in Φ, the Fermi level shifts toward the midgap, and, consequently, the carrier removal rate by point defects in the conducting matrix is also decreased.

The dependence of $n_{\rm eff}$ on the fluence Φ and temperature T can be written as [6]

$$n_{\rm eff}(T,\Phi) = n(T,\ \Phi)(1 - f(T,\ \Phi)), \quad (2)$$

where $n(T,\Phi)$ is the carrier concentration in the conducting matrix of n-Si.

Therefore, based on the Gossick's corrected model [7] and taking into account the capture of carriers on the deep levels of defects in the conducting matrix, we may calculate $n_{\rm eff}$. In more details, the technique of calculations of $n_{\rm eff}$ was presented in [8].

It is known that the annealing leads to the recovery of solid characteristics. To study the kinetics of the interaction of radiation defects, it is very important to determine their activation energy and the frequency of jumps. To describe the annealing process, one usually uses the equations of the kinetics of chemical reactions [2]. It is supposed that the defect must obtain the energy $E_{\rm a}$ to realize a reaction. At the temperature T, the fraction of such defects is defined by the exponential Boltzmann factor $\exp(-E_a\ /\ kT)$, and the concentration of defects is described by the equation

$$N(t) = N_0 \exp\left[-\nu\ t\ \exp\left(-\frac{E_a}{kT}\right)\right], \quad (3)$$

where $N(t)$ and E_a are the concentration and the activation energy of defects, respectively; N_0 is the initial concentration of defects; ν is the frequency factor (the jump number of defects per second); t is the annealing duration; k is the Boltzmann constant; and T is the annealing temperature.

The annealing of defects can be investigated, by determining $n_{\rm eff}(T,\Phi)$ by the calculation of the concentration of carriers removed in the conducting matrix $n(T,\Phi)$ both by point defects and by clusters $n_{\rm cl}(T,\Phi)$. The calculation of the dependence of $n_{\rm cl}$ on the annealing time (t) was carried out for the process of isothermal annealing of the Si⟨Ge⟩ samples irradiated with the fluence Φ.

4. Isothermal Annealing of Si⟨Ge⟩

We performed the study of the isothermal annealing of Si⟨Ge⟩ samples initially irradiated with a fluence of 1.4×10^{14} neutr./cm^2 of fast-pile neutrons at various temperatures (20, 80, and 106 °C). The dependences of the carrier concentration removed by defect clusters from the conduction band, ($n_{\rm cl}$), on the annealing duration t are presented in Fig. 1.

The experimental data (Fig. 1) can be described by the equation of annealing kinetics (3), if the presence of

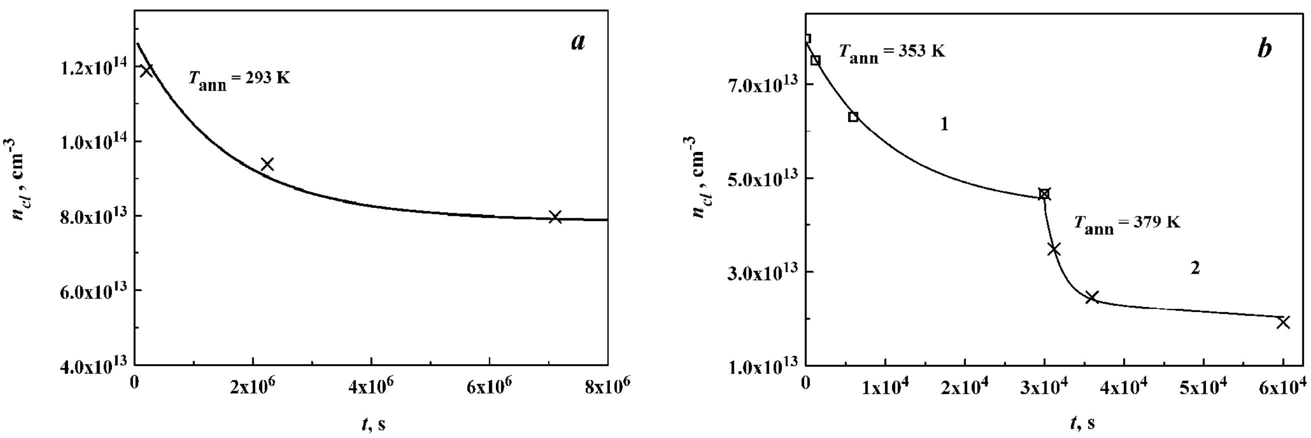

Fig. 1. Dependences of the carrier concentration removed by defect clusters $n_{\rm cl}$ on the annealing duration t in Si⟨Ge⟩: a — at room temperature; b — at 80 (*1*) and 106 °C (*2*). The initial fluence of fast-pile neutrons Φ is 1.4×10^{14} neutr./cm^2. Daggers and squares present the experimental data; solid lines present the theoretical calculations

"fast" and "slow" components of the annealing is supposed. In this case,

$$n_{\rm cl}(t) = n_{01}\ \exp\left[-\nu_1\, t\ \exp\left(-\frac{E_1}{kT}\right)\right]+$$

$$+n_{02}\ \exp\left[-\nu_2\, t\ \exp\left(-\frac{E_2}{kT}\right)\right], \qquad (4)$$

were $n_{01},\ n_{02}$ are the number of carriers removed from the conduction band after irradiation due to the formation of V_3 and V_2, respectively; E_1 and $E_2$are the activation energies of the vacancy defect annealing (V_3 and V_2); ν_1 and ν_2 are the frequency factors of the annealing process.

As a result of the calculation of $n_{\rm cl}(t)$ by Eq. (4), the following values were obtained: $E_1 = 0.74$ eV, $\nu_1 = 3.5 \times 10^6$ s^{-1} and $E_2 = 0.91$ eV, $\nu_2 = 7 \times 10^6$ s^{-1}. These parameters well describe the annealing at all three temperatures ($T_{\rm ann}$).

It is known [9] that the concentration of A-centers (VO) increases under the annealing of silicon irradiated by fast neutrons. Since V_2 and V_3 are the main defects in clusters, the annealing of these defects leads to the vacancy generation (V) and can be described by the following reactions:

$$V_2 + I \to V; \quad V_3 + I_2 \to V. \qquad (5)$$

In this case, we suppose that vacancy-type defects interact not only with interstitials (I), but also with di-interstitials (I_2).

If the vacancy-type defects are usually concentrated in clusters, then the interstitial-type defects are concentrated in the conducting matrix. It is the high concentration of oxygen in the studied Cz-Si and Si⟨Ge⟩ samples that leads to the increase of the interstitial defect concentration in the conducting volume. As shown in [10], oxygen prevents the exit of Si interstitial atoms into the crystal surface and, probably, is a center of the di-interstitial defect formation. In [11, p. 820], it was supposed that, under a high density of interstitial atoms in the matrix, they form Si—Si pairs. Such pairs appear as a result of the stochastic hitting of two silicon atoms into the one interstitial space. These pairs are kept in the one interstitial space only by the potential relief of the crystal, without the formation of chemical covalent bonds between Si atoms.

We suppose that the annealing of clusters occurs at the expense of the direct annihilation of I and I_2 with vacancy defects (V_2 and V_3), according to reactions (5). Then, if the activation energy of migration $E_1 = 0.74$ eV and the frequency factor $\nu_1 = 3.5 \times 10^6$ s^{-1} (the "fast" component in Eq. (4)) are attributed to di-interstitials; and $E_2 = 0.91$ eV and $\nu_2 = 7 \times 10^6$ s^{-1} (the "slow" component) are attributed to silicon interstitial atoms, we obtain the good correspondence between the results of calculations and experimental data. In the offered annealing model, we supposed that di-interstitials are more mobile (the activation energy and the frequency factor are smaller), than interstitial atoms. The activation energy of oxygen dimers by 0.8 eV is less than that of a single oxygen atom [12]. Moreover, according to [11], Si—Si di-interstitials are more mobile than a single Si interstitial atom. In [13,14], the values of activation energies of the interstitial atom and the vacancy are near 1 eV.

It can be supposed that the sizes of larger clusters grow at the expense of the decay of smaller clusters. This supposition is based on the obtained data concerning the determination of the concentration and the average size of defect clusters after the isothermal annealing. The temperature dependence of the effective kinetic coefficients allows one to determine not only the number of carriers removed by defect clusters, but also the number of defect clusters and their average sizes. The behavior of defect clusters under the annealing (a change of their sizes) corresponds to the fact that the concentration of divacancies in a mid-size cluster is (2—2.5) times higher than the concentration of trivacancies, and the concentration of small-size clusters is ∼2 times higher than othatne of mid-size clusters. It is known that V_3 defects are annealed at 250 °C and V_2 – at 350 °C [15]. It should be noted that the annealing temperatures in our experiments were substantially smaller, than the annealing temperatures for V_3 and V_2.

To describe the above process of cluster annealing, we use the equation

$$n_{\rm cl}(t) = n_{01}\ \exp\left[-\nu\ t_1\ \exp\left(-\frac{E}{kT_1}\right)\right]+$$

$$+n_{02}\left[1-\exp\left(-\nu\ t_1\ \exp\left(-\frac{E_{\rm V}}{kT_1}\right)\right)\right], \qquad (6)$$

where n_{01} is the number of carriers returned into the conduction band at the expense of the annealing of small clusters; and n_{02} is the number of carriers captured from the conduction band by large clusters.

The first term of Eq. (6) describes the annealing of vacancy-type defects in small-size clusters, while such an annealing in Eq. (4) is specified as the annealing due to the annihilation of interstitials and di-interstitials with vacancy-type defects (V_2 and V_3), according to reactions (5). In this case, the generation of vacancies occurs. Such free vacancies are captured by other clusters with the formation of defects due to bimolecular reactions, for example, V_2+V→V_3 and V_3+V→V_4. Thus, the second term of Eq. (6) describes the increase of the number of carriers removed by the residuary clusters. Since V_3 and V_4 defects have deeper levels in the forbidden band of the semiconductor [16], the level population is increased, and, consequently, the number of carriers removed by residuary clusters is increased in the course of the isothermal annealing. Using this model of the annealing, we obtain $E_{\rm V} = 0.8$ eV for the activation energy of vacancies and the frequency factor $\nu = 1 \times 10^7$ s^{-1}. The obtained activation energy of interstitial-type defects

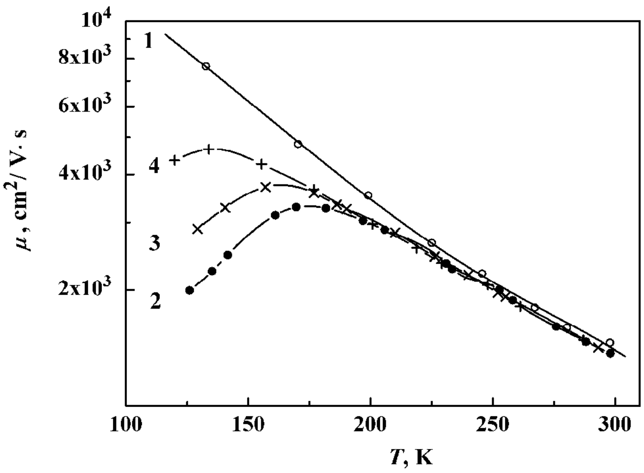

Fig. 2. Temperature dependences of the carrier mobility μ in n-type Cz-Si ($n_0 = 5.02 \times 10^{13}$ cm^{-3}) before (*1*) and after the irradiation by fast neutrons: *2* — the fluence $\Phi = 2\times 10^{13}$ neutr./cm^{-2}; *3, 4* — the same fluence and the added dose of gamma irradiation: *3* — $\Phi_{\gamma 1} = 3 \times 10^6$ R; *4* — $\Phi_{\gamma 2} = 1.2 \times 10^7$ R; ∘, •, +, × are the experimental data

($E = 0.795$ eV) is equal to the average value of activation energies, namely 0.91 and 0.74 eV, used under the improved description of the annealing, according to reactions (5). The frequency factor (ν) can be considered as the sum of frequency factors, namely 3.5×10^6 and 7×10^6 s^{-1}, obtained in the same process (4). In such a description, it is supposed that vacancies released from a cluster are captured by other clusters, rather than by impurities (for example, by oxygen), since the capture radius is near 5 Å for impurities and several hundreds of angstroms for clusters.

5. Radiation Annealing of n-type Cz-Si

It is natural to suppose that the additional ^{60}Co gamma irradiation of Cz-Si samples should lead to increasing the volume part occupied by cluster defects due to the additional introduction of deep-level point defects.

The study of the influence of the additional gamma irradiation by ^{60}Co was carried for the n-type Cz-Si samples ($n_0 = 5.02 \times 10^{13}$ cm^{-3}) which were preliminarily irradiated by fast-pile neutrons with $\Phi =$ $= 2\times 10^{13}$ neutr./cm^{-2}. Figure 2 shows the temperature dependences of the carrier mobility μ before and after irradiation.

In [17], it was shown that, under the irradiation by fast-pile neutrons, the temperature, at which the maximum of the carrier mobility is observed, is related to the fluence Φ. Such a temperature named "critical" ($T_{\rm cr}$) is linearly shifted with increase in the fluence to the region of room temperature and is well described by the empirical equation

$$T_{\rm cr} = \frac{\Phi}{A n_0^{5/6}}, \tag{7}$$

where A is the coefficient of proportionality, n_0 is the carrier concentration at room temperature before irradiation. For the n-type Cz-Si samples, A is approximately 0.44 [18].

In [19], it was shown that $T_{\rm cr}$ determines a part of the volume occupied by defect clusters. With increase in the fluence, this volume part linearly grows due to the introduction of point defects. This dependence is described by $f = \Sigma V \Phi$ and is similar to the linear growth of $T_{\rm cr}$ with Φ (7). Then $f = T_{\rm cr} \Sigma V A n_0^{5/6}$. Consequently, using the dependence of $T_{\rm cr}$ on the gamma irradiation dose, a change of the volume part occupied by defect clusters can be estimated. As a result of the carried out calculations, it was obtained that, after the irradiation with $\Phi_{\gamma 1}$= 3 $\times$ 10^6 R, the decrease of the volume part occupied by defect clusters is near 10 %, and, for $\Phi_{\gamma 2} = 1.2 \times 10^7$ R, this value increases up to 23 %. The decrease of the cluster volume part evidences for the γ-irradiation annealing.

Under gamma irradiation of silicon, the electrons are knocked out with energy that is higher than the threshold energy for the atom displacement. In turn, this leads to the generation of simple point defects (vacancies and interstitials) on various distances from one another. Under irradiation, the interstitial silicon atoms have small activation energy for migration. Therefore, the interstitial and di-interstitials atoms earlier created by fast-pile neutrons will be captured in clusters under gamma irradiation and directly recombine with vacancies by reactions (5).

In Cz-Si, the high oxygen concentration suppresses the introduction of new E-centers (PV) due to the vacancy capture by oxygen. It is known that, under gamma irradiation, the divacancies are formed only by the association of single vacancies [20] (as a secondary defect), which is also suppressed due to a high oxygen concentration. Therefore, under gamma irradiation, the conducting matrix will be less deformed due to the deep levels of E-centers and divacancies.

Thus, the observed effect of the defect cluster annealing (a decrease of the volume part occupied by defect clusters) under gamma irradiation can be explained by the above-mentioned processes.

6. Conclusions

It is shown that, at the temperatures of 20, 80, and 106 °C, the annealing of defect clusters after the irradiation of Si⟨Ge⟩ by fast neutrons is caused by the annihilation of vacancy-type defects with interstitial atoms and di-interstitials. We have determined the activation energy and the frequency factor for di-interstitials ($E_1 = 0.74$ eV and $\nu_1 = 3.5 \times 10^6$ s^{-1}), interstitial silicon atoms ($E_2 = 0.91$ eV и $\nu_2 = 7 \times 10^6$ s^{-1}), and vacancies ($E_{\rm V} = 0.8$ eV, $\nu = 1 \times 10^7$ s^{-1}).

It is shown that, in the n-type Cz-Si samples ($n_0 = 5.02 \times 10^{13}$ cm^{-3}) preliminarily irradiated by fast-pile neutrons, the radiation annealing is observed under the ^{60}Co gamma irradiation. In this case, the decrease of the volume fraction occupied by defect clusters after the gamma-irradiation dose of $\Phi_{\gamma 1} = 3 \times 10^6$ R is nearly 10 % and about 23 % for the gamma-irradiation dose of $\Phi_{\gamma 2} = 1.2 \times 10^7$ R.

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ВІДПАЛ КЛАСТЕРІВ ДЕФЕКТІВ У ЗРАЗКАХ Si ТА Si⟨Ge⟩, ВИРОЩЕНИХ МЕТОДОМ ЧОХРАЛЬСЬКОГО

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Р е з ю м е

Досліджено зразки кремнію n-типу провідності, вирощеного методом Чохральського (Cz-Si), з домішкою германію ($N_{\rm Ge} = 2 \cdot 10^{20}$ см$^{-3}$) та без неї після опромінення швидкими нейтронами реактора. Проведено вивчення відпалу n-Si⟨Ge⟩ після опромінення флюенсом $1{,}4 \cdot 10^{14}$ нейтр./см^2 при трьох температурах. Показано, що відпал кластерів дефектів пов'язаний з анігіляцією дефектів вакансійного типу у кластерах з міжвузловинними дефектами. Розглянуто відпал кластерів дефектів у нейтронно-опромінених зразках Cz-Si n-типу під дією γ-квантів.