Vacancy-donor pairs and their formation in irradiated *n*-Si

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The present experiments using fast electron and gamma-irradiation are aimed at checking the model of defect formation in oxygen-lean *n*-Si(FZ) in a quantitative way. Electrical measurements are taken over a wide temperature range of 20 to 300 K. Analysis of equations of charge balance making use of the statistics of charge carriers in non-degenerate semiconductors demonstrates that group-*V* impurity atoms strongly interact with intrinsic point defects. As a result, the concentration of shallow donor states is markedly decreased. This loss of shallow donors, $-\delta N_D$, is accompanied with an increase in the concentration of radiation-produced deep acceptors, $+\delta N_A^{\rm rad}$, being equal in magnitude but opposite in sign. Such behavior correlates quantitatively with the formation model of donor–vacancy pairs put forward earlier by Watkins and Corbett, what has been proved on the basis of electrical data for the first time. The formation kinetics of these complexes is discussed. Defects of interstitial type in irradiated material appear to be electrically neutral in *n*-Si. However, their production in the course of electron- and gamma-irradiation is believed to be responsible for drastic changes in the mobility of charge carriers at cryogenic temperatures.

1. Introduction

Structural defects produced in Si during irradiation with fast electrons have been studied by means of various techniques in detail. Dominant vacancy-related defects in irradiated *n*-Si determining changes in electrical properties are well-known. These are pairs vacancy–oxygen, the so-called *A*-centers, in oxygen-rich *n*-Si [1,2] and vacancy–group-V impurity atom, the so-called *E*-centers, in oxygen-lean *n*-Si [1,3,4]. In spite of a great body of information on these defects collected in literature so far, some un-expected features of the centers seemingly investigated in considerable detail are making their appearance from time to time. By way of example, the *E*-centers being known as deep acceptors at $\sim E_C - 0.4$ eV for a long time was recently found to be amphoteric, also having donor states at $\sim E_V + 0.27$ eV [5]. Conducting investigations of electri-cally active defects in proton-irradiated oxygen-lean *n*-Si one needs as a reference the data of Hall effect measurements carried out on the identical material irradiated with fast electrons. Searching the literature available so far one cannot find reliable information on electrical properties of electron-irradiated *n*-Si using Hall effect measurements at cryogenic temperatures, down to $T \approx 20$ K. At the same time, it has been known that such measurements furnish comprehensive data on concentrations of shallow donor states of group-V impurities and compensating acceptors being related to formation processes of radiation defects. As a matter of fact, there is no direct comparison of losses of shallow donor states, $-\delta N_D$, due to the *E*-center formation and changes in the concentration of radiation-induced acceptors, $+\delta N_A^{\rm rad}$, based on electrical measurements in irradiated *n*-Si. In this respect, it should be mentioned that a relative comparison

of changes in the concentrations of shallow donors and *E*-centers was earlier made in [1] with the aid of calibration of the intensities of relevant EPR lines, within the limits of error by a factor of 1.5 to 2. If the formation of *E*-centers is an absolutely dominating defect reaction in irradiated *n*-Si, so one can expect $|-\delta N_D| \approx \delta N_A^{\rm rad}$. Otherwise, it should mean that there are some additional reactions between group-V impurity atoms and intrinsic defects running at significant reaction rates.

The present paper is aimed at checking the relation between $-\delta N_D$ and $+\delta N_A^{\rm rad}$ in oxygen-lean *n*-Si subjected to irradiation with electrons at ~ 1 MeV. Together with this, it is of keen interest to get a look at the charge carrier mobility in irradiated materials.

2. Experimental

In accordance with the aim, square-shaped samples were cut from *n*-Si ingots grown by the floating-zone technique, *n*-Si(FZ). The doping level with phosphorus was close to $1 \cdot 10^{16}$ cm^{-3}. This concentration is similar to those in *n*-Si(FZ) samples earlier used in EPR measurements [1,3,4].

To suppress contributions of various multi-vacancy com-plexes, samples were irradiated with electrons at 0.9 MeV in a resonant transformer accelerator on a target in a water stream. The characteristic parameters of pulsed irradiation were as follows: the pulse repetition frequency was 490 Hz and the pulse duration was 330 μs. The averaged intensity of electron irradiation is $I = 7.5 \cdot 10^{13}$ electrons/cm$^2 \cdot$ s. The irradiation temperature did not exceed 30°C to prevent defect annealing. Together with this, some samples were irradiated with gamma-rays of ^{60}Co at 1.25 MeV at room temperature. The intensity of gamma-irradiation was $1 \cdot 10^{12}$ gamma-quanta/cm$^2 \cdot$ s. Under such irradiation

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<mark>conditions, host atoms are mainly displaced from their lattice sites by the Compton electrons at an averaged energy of 700 keV.</mark> In other words, this is equivalent to internal irradiation with fast electrons in the bulk samples.

Electrical measurements of the electron concentration n and mobility μ_e in n-Si(FZ) samples before and after irradiation were taken with the help of the Van der Pauw technique over a wide temperature range from $T \approx 20$ K to 300 K, thus producing experimental curves of $n(1/T)$ and $\mu_e(T)$ over the entire temperature interval of extrinsic conductivity due to ionization of shallow donors. Electrical measurements of this kind are conducted under thermal equilibrium conditions, so the Fermi level F governs the occupancy of all donor and acceptor states in the studied material. As a result, in non-degenerate semiconductors like the n-Si(FZ), $n(1/T)$ curves can be analyzed by means of a simple equation of charge balance in respect to F using the statistics of charge carriers; see Eq. (1) and also for details in [6]:

$$\frac{n(n+N_A)}{N_D-N_A-n} = N_C \frac{\exp(-E_D/kT)}{2+10\exp(-\Delta/kT)}, \quad (1)$$

where n is the concentration of free electrons in the conduction band; N_D and N_A are the *total* concentrations of shallow group-V donor states and deep acceptors, respectively; N_C is the effective density-of-states in the conduction band; E_D is the ionization energy of the singlet ground states of group-V impurity atoms and Δ is the splitting of the singlet-(doublet + triplet) ground states. The splitting between the doublet and triplet ground states is ingnored in (1) because of its much lesser value as compared to Δ. All concentration terms in (1) are temperature-dependent. The total concentration N_A is equal to the initial concentration of all acceptors before irradiation, N_A^0, and $N_A^0 + N_A^{\mathrm{rad}}$ after irradiation, where N_A^{rad} is the total concentration of all radiation-induced acceptors; changes in $N_A^0 + N_A^{\mathrm{rad}}$ will be discussed below. The value of Δ is taken from optical measurement [7]. The effective mass of electrons in the conduction band, defining N_C, is known from cyclotron resonance experiments [8,9].

If $n \ll N_D$ and N_A, from an exponential part of $n(1/T)$ curves of Eq. 1 one can determine the compensation ratio $K = N_A/N_D$ at $T = 0$ K. Values of N_D include all the shallow donor states available at $T = 0$ K, no matter filled with electrons as well as empty of electrons due to partial compensation by the acceptors N_A. From the other side, the electron concentration n_{sat} at the saturation plateau of extrinsic conductivity is equal to $n_{\mathrm{sat}} = N_D - N_A$. Knowing K and n_{sat} one can separately determine both N_D and N_A. For deeper centers whose energy states in the upper half of the band gap are completely filled with electrons at $T = 0$ K, they can be seen on $n(1/T)$ curves when the Fermi level is shifted to them with increasing temperature. In our case the acceptor states of E-centers are deep enough, so they are completely filled with electrons even at room temperature. Large errors in estimation of N_D and N_A values may be introduced by the exponential term containing E_D. This

point in electrical measurements at cryogenic temperatures has usually received much attention. Variations of E_D in calculations were taken in steps of 0.5 meV, defining the effective ionization energy of shallow donors. This factor may introduce changes in absolute values of N_D and N_A by ten percent. One should take into account that the both concentrations are related by K and n_{sat}, the conclusions drawn on their relative changes due to irradiation hold true.

3. Results and discussion

As an illustration of a typical sample, Fig. 1 shows the concentration of charge carriers in the n-Si(FZ) before and after electron irradiation over the entire temperature range studied. The compensation ratio of the initial material was found to be very small, $K = N_A/N_D \approx 0.01$ and less. It means that the initial material was weakly compensated and $N_A^0 \ll 1 \cdot 10^{14}$ cm^{-3}, so one can ignore the contribution of residual acceptors to $(N_A^0 + N_A^{\mathrm{rad}})$. In actual fact, N_A^{rad} is greater than $1 \cdot 10^{15}$ cm^{-3} at all irradiation doses in the present experiments. In the course of electron irradiation the concentration of charge carriers drops as the irradiation dose Φ is increased; see Fig. 1. Reaching the saturation plateau after irradiation the concentration of charge carriers doesn't change at $T > 100$ K anymore. One could expect such an effect, since the negatively charged acceptor states of E-centers are deep enough to get neutral at the Fermi level $F \approx E_C - 0.25$ eV at room temperature, estimated for the n-Si(FZ) at $\Phi = 3 \cdot 10^{16}$ electron/cm^2; see Fig. 1.
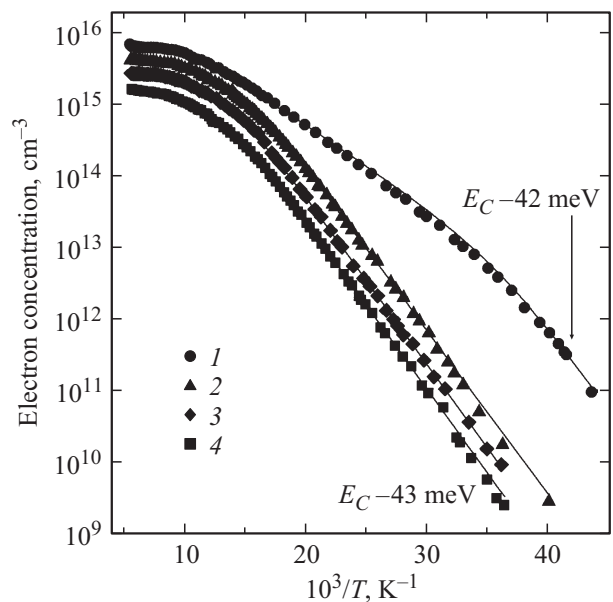

Figure 1. Charge carrier concentration *versus* reciprocal temperature for the n-Si(FZ) irradiated with 0.9 MeV electrons at room temperatures. Points, experimental; curves, calculated. Irradiation dose Φ, electrons/cm^2: 0 (*1*); $1 \cdot 10^{16}$ (*2*); $2 \cdot 10^{16}$ (*3*); $3 \cdot 10^{16}$ (*4*). Effective ionization energies of shallow donors are indicated.
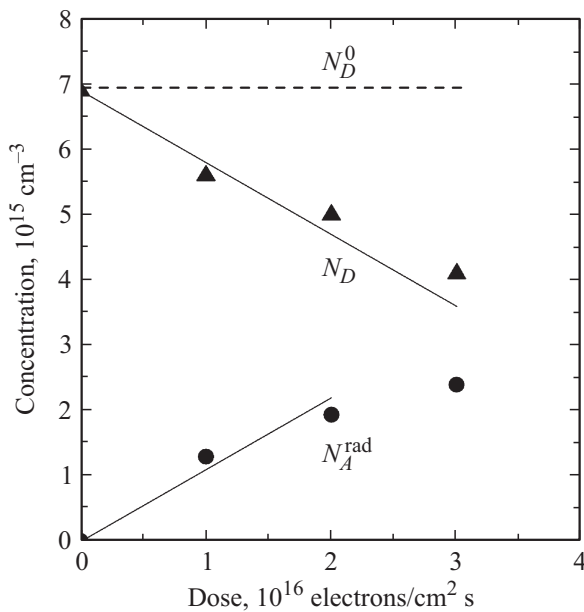
Figure 2. Changes in the total concentrations of shallow donors and compensating acceptors in the *n*-Si(FZ) *versus* irradiation dose Φ. Irradiation with 0.9 MeV at room temperatures. N_D^0 is the total concentration of shallow donors before irradiation (dashed line). The kinetics of $N_D(\Phi)$ can be approximated by Eq. (4); see text.

Analysis of the curves $n(1/T)$ in Fig. 1 demonstrated a reliable 1 : 1 correspondence between the loss of shallow donor states and concentration of radiation-induced acceptors at all the irradiation doses, thus providing convinced evidence of the formation of E-centers; see Fig. 2. It is just the defect reaction one can expect to take place under irradiation. Actually, irradiation can produced in Si simple native defects like isolated vacancies and self-interstitials. Pairing of group-V impurity atoms with free vacancies mobile at room temperature leads to loss of shallow donor states, on one hand, and formation of E-centers, on the other hand. This reaction is enhanced because of the Coulomb attraction between positively charged group-V impurity atoms, D^+, and negatively charged vacancies, most likely V^{2-} [10]. The self-interstitial reaction paths are believed to be different: they may form di-interstitial pairs or pairs with residual carbon and oxygen atoms. However, it should be stressed that the $n(1/T)$ curve for the *n*-Si(FZ) sample irradiated at $\Phi = 3 \cdot 10^{16}$ electron/cm^2 displays a plateau at $100\,\mathrm{K} \le T \le 300\,\mathrm{K}$, with the Fermi level shifting from $E_C - 0.07\,\mathrm{eV}$ to $E_C - 0.26\,\mathrm{eV}$. It means that there no significant concentrations of carbon- and oxygen-related energy states in the energy interval indicated above, within the limits of error, i e being equal to or smaller than $2 \cdot 10^{14}\,\mathrm{cm}^{-3}$. Our results tell us that most secondary interstitial-related defects must be neutral in *n*-Si(FZ), since the radiation-produced compensation is found to be mostly due to the E-center formation, within an accuracy of ten

percent. The same conclusions can also be drawn for the gamma-irradiated *n*-Si(FZ); see Fig. 3 and 4.

Let us briefly discuss the kinetics of defect reactions in electron-irradiated *n*-Si(FZ); some details of earlier
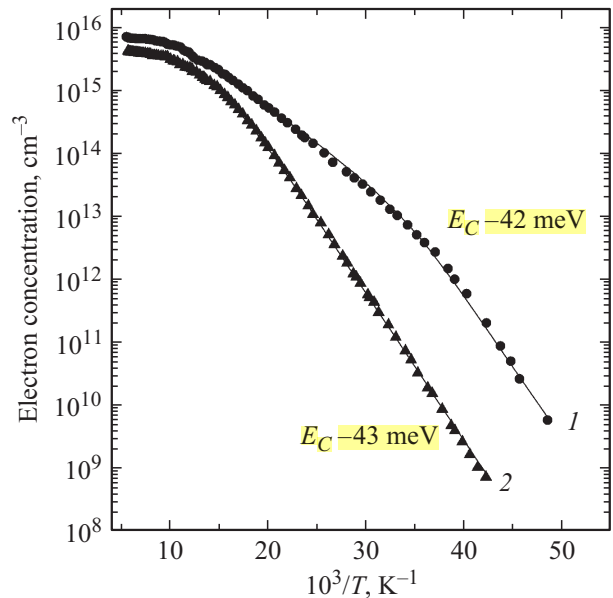

Figure 3. Charge carrier concentration *versus* reciprocal temperature for the *n*-Si(FZ) irradiated with ^{60}Co gamma-rays at room temperatures. Points, experimental; curves, calculated. Irradiation dose Φ, gamma-quanta/cm^2: 0 (*1*); $4.6 \cdot 10^{17}$ (*2*). Effective ionization energies of shallow donors are indicated.
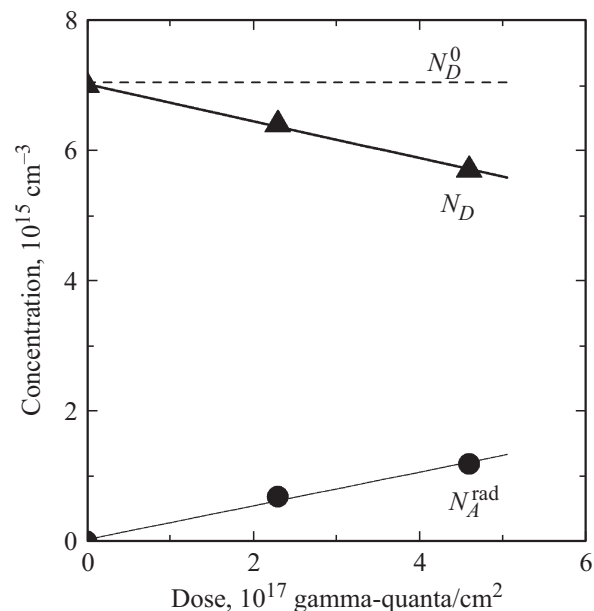

Figure 4. Changes in the total concentrations of shallow donors and compensating acceptors in the *n*-Si(FZ) *versus* irradiation dose Φ. Irradiation with ^{60}Co gamma-rays at room temperatures. N_D^0 is the total concentration of shallow donors before irradiation (dashed line). The kinetics of $N_D(\Phi)$ can be approximated by Eq. (4); see text.

discussion see in [11]. Taking into consideration the results given above, one can write the following equations related to the production of vacancies and their reaction with shallow donors:

$$\frac{dN_V}{dt} = \lambda - \gamma N_V N_D, \tag{2a}$$

$$\frac{dN_D}{dt} = -\gamma N_V N_D, \tag{2b}$$

where N_V is the concentration of vacancies pairing with group-V impurity atoms; N_D is the concentration of free group-V impurity atoms; λ is the production rate of primary defects; γ is the reaction constant. The production rate is equal to $\lambda = \sigma I N_{Si}$ where σ is the cross-section of production of Frenkel pairs, I is the intensity of irradiation, and N_{Si} is the concentration of host atoms in Si, $N_{Si} = 5 \cdot 10^{22}\,\mathrm{cm}^{-3}$. The initial rate of formation of E-centers is found to be $\eta_E = 0.11\,\mathrm{cm}^{-1}$. This value is very close to the rate of formation of A-centers (vacancy–oxygen atom pairs) in oxygen-rich n-Si irradiated with fast electrons at $1\,\mathrm{MeV}$, $\eta_A \approx 0.1\,\mathrm{cm}^{-1}$ [12]. Such a good agreement of the rates in n-Si with similar phosphorus concentrations allows one to take this value as an effective rate of the vacancy production. In other words, $\lambda_{\mathrm{eff}} = \sigma_{\mathrm{eff}} I N_{Si} = \eta_E I = 8.25 \cdot 10^{12}\,\mathrm{cm}^{-3} \cdot \mathrm{s}^{-1}$. Therefore, making use of the effective rate one can consider only a fraction of vacancies taking part in pairing with shallow donors; in this way other defect reactions, e g direct annihilation with self-interstitials in Frenkel pairs and so on, may be moved sideways.

The reaction constant can be estimated as $\gamma = \alpha\beta$ where α and β are proportional to the probability of encounter of a vacancy with an impurity atom and the probability of formation of a pair, respectively. Taking the dimensions of terms in Eq. (2a) and (2b) into account, the first coefficient may be set as $\alpha = a^3 v \exp\left(-E_V^m/kT\right)$ where a is the lattice spacing, $v \approx 1 \cdot 10^{13}\,\mathrm{s}^{-1}$ is the vibration frequency of lattice atoms, and $E_V^m = 0.18\,\mathrm{eV}$ [10] is the activation energy of migration of a free vacancy V^{2-} in the Si lattice. α is equal to volume V across which a vacancy is moving per unit time. Of course, the vibration modes in the vicinity of a vacancy are believed to be softened as compared to the crystal lattice. However, in the present order-of-magnitude estimates it seems not to be of critical importance. As a result, one obtains $\alpha \approx 1.2 \cdot 10^{-12}\,\mathrm{cm}^3 \cdot \mathrm{s}^{-1}$. The second coefficient may be set as $\beta = \exp(-E_{\mathrm{barrier}}/kT)$ where E_{barrier} is the energy barrier for formation of a defect pair. In our case of pairing D^+ and V^{2-} it is reasonable to suggest $\beta = 1$.

The initial conditions for Eq. (2a) and (2b) are $t = 0$, $N_V = 0$, and $N_D = N_D^0$ where N_D^0 is the initial concentration of shallow donors. To solve these equations is possible by introducing two dimensionless parameters: $\xi = \lambda/\gamma(N_D^0)^2$ and $\vartheta = \gamma N_D^0 t$. Making use of these parameters the solution
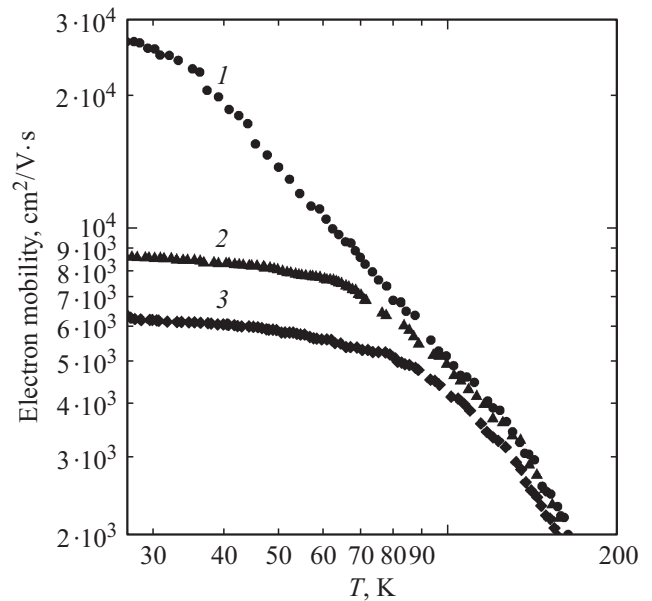

Figure 5. Charge carrier mobility *versus* temperature for the n-Si(FZ) irradiated with 0.9 MeV electrons at room temperatures. Points, experimental. Irradiation dose Φ, electrons/cm²: 0 (*1*); $1 \cdot 10^{16}$ (*2*); $3 \cdot 10^{16}$ (*3*).

can be obtained in the following form:

$$N_D = N_D^0 \frac{\exp\left[(-\xi\vartheta^2/2) + \vartheta\right]}{1 + \int_0^\vartheta \left[\exp(-\xi S^2/2) + S\right]dS}. \tag{3}$$

The concentration of E-centers is equal to $N_E = N_D^0 - N_D$. In general, the time-dependent N_D appears to be nonlinear. In our case $\xi = \lambda/\gamma(N_D^0)^2 = 1.4 \cdot 10^{-7}$, i.e. $\xi \ll 1$, the expansion of Eq. (3) in terms of the Taylor series gives

$$N_D/N_D^0 = 1 - \xi\vartheta + \xi - \xi\exp(-\vartheta), \tag{4}$$

retaining the first two terms in the expansion. Under our irradiation conditions, the two last terms in Eq. (4) can be neglected for $\vartheta < 1/\xi$. Therefore, the kinetics of N_D appears to be linear at early stages of irradiation. This is clearly seen in Fig. 2. At $\Phi = 3 \cdot 10^{16}$ electrons/cm² it can be shown that the condition of linearity is not satisfied anymore. It should be noted that at this point the compensation ratio of shallow donors in irradiated samples is $K \approx 0.6$.

In the case of gamma-irradiation the values of ξ appears to be much less than those in the case of electron irradiation, so the consideration given above holds true as well. As is seen in Fig. 4, the kinetics of N_D in the gamma-irradiated n-Si(FZ) is also proportional to Φ. In this case the effective removal rate of N_D was found to be $2.6 \cdot 10^{-3}\,\mathrm{cm}^{-1}$.

The last point to be discussed is related to changes in the mobility of charge carriers in irradiated n-Si(FZ). One could expect that the electron mobility should be relatively insensitive to increasing irradiation dose, for
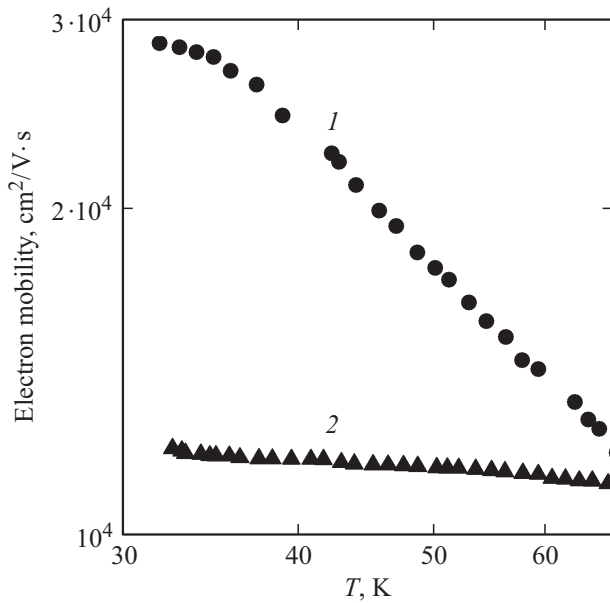
Figure 6. Charge carrier mobility *versus* temperature for the n-Si(FZ) irradiated with ^{60}Co gamma-rays at room temperatures. Points, experimental. Irradiation dose Φ, gamma-quanta/cm^2: 0 (*1*); $4.6 \cdot 10^{17}$ (*2*).

the formation of E-centers shouldn't markedly change the concentration of ionized scattering centers. In actual fact, the observed loss of shallow donors as scattering centers of charge carriers due to irradiation is accompanied with the same increase in the E-center concentration; see Fig. 2 and 4. This behavior is true for moderately doped n-Si(FZ) at temperatures $300 \geq T \geq 100$ K, i.e. at the saturation plateau of electron conductivity where the total concentration of ionized scattering centers in irradiated material equals $N_{\rm ion} = (N_D^0 - |\delta N_D|) + \delta N_A^{\rm rad} \approx N_D^0$ because of $|-\delta N_D| \approx \delta N_A^{\rm rad}$. As a result, the electron mobility in n-Si(FZ) after irradiation remains practically unaltered over a temperature interval of $100 \leq T \leq 300$ K, as compared to that before irradiation. Here a certain disparity between the scattering cross-section of positively and negatively charged centers is ignored. However, at lower temperatures, down to $T \approx 30$ K, the uncompensated donors ($N_D - N_A^{\rm rad}$) become neutral, so the total concentration of ionized centers $N_{\rm ion} = (2N_A^{\rm rad} + n)$, where $n \ll N_A^{\rm rad}$, is growing as the irradiation dose increases. In view of the increasing $N_{\rm ion} \approx 2N_A^{\rm rad}$ at lower temperatures one can expect a marked drop of the electron mobility in n-Si(FZ) with increasing dose. As is shown in Fig. 5, after irradiation the mobility of charge carriers in the electron-irradiated n-Si(FZ) does drop but the shape of the $\mu_e(T)$ curves at $T < 70$ K appears to be strange. Actually, the charge carrier scattering due to ionized centers usually shows itself as some pronounced changes in $\mu_e(T)$ curves with a slope close to $T^{3/2}$ at very low temperatures, $T \leq 40$ K; see for instance [13–15]. Instead, one can see a weak temperature dependence of the electron mobility, $\mu_e \propto T^{-1/6}$ over a

wide temperature interval of 25 K $\leq T \leq 60$ K. No doubt, the observed changes in the dose-dependent mobility are associated with radiation- produced defects. Similar observations have also been made in the case of n-Si(FZ) irradiated with gamma-rays; see Fig. 6. We believe that such effects may be due to large-scale deformations induced by radiation defects in the crystal lattice. A hint in this respect might be taken from the mobility of charge carriers being $\mu_e \propto T^{-1/2}$ at 25 K $\leq T \leq 40$ K in n-Si$_{1-x}$Ge$_x$ alloys at $x = 0.008$ [16] with such deformations in the Si lattice are related to substitutional Ge atoms. Interestingly, in our case an effect of the disturbance of the Si lattice upon the electron mobility is thought to be rather related to radiation defects of interstitial-type than to those containing vacancies. This intriguing question needs further investigations.

4. Conclusions

The Hall effect measurements taken on oxygen-lean n-Si over a wide temperature range clearly show a $1:1$ correspondence between the loss of shallow donors and concentration of radiation-produced deep acceptors under fast electron- and gamma irradiation. This is sufficient demonstration that the E-center formation is an absolutely dominating defect reaction between group-V impurity atoms and vacancies in such moderately doped materials. It also means that other possible complexes with group-V impurities [17] are of subsidiary importance in the present experiments. Together with this, the data obtained point to the fact that self-interstitials and/or interstitial-related defects, being produced simultaneously with vacancies at the same rate, are mostly electrically neutral in n-Si. On the other hand, strong changes of the mobility of charge carries in irradiated materials are believed to be associated with interstitial-related defects giving rise to large-scale elastic deformations in the crystal lattice.

Acknowledgments

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