

Some challenging points in the identification of defects in floating-zone *n*-type silicon irradiated with 8 and 15 MeV protons

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Electrical properties of defects formed in *n*-Si(FZ) following 8 and 15 MeV proton irradiation are investigated by Hall effect measurements over the wide temperature range of $T \approx 25$ to 300 K. Close attention is paid to the damaging factor of proton irradiation, leaving aside passivation effects by hydrogen. The concept of defect production and annealing processes being accepted in the literature so far needs to be reconsidered. Contrary to expectations the dominant impurity-related defects produced by MeV protons turn out to be electrically neutral in *n*-type material. Surprisingly, radiation acceptors appear to play a minor role. Annealing studies of irradiated samples of such complex defects as a divacancy tied to a phosphorus atom and a vacancy tied to two phosphorus atoms. The latter defect features high thermal stability. Identification of the dominant neutral donors, however, remains unclear and will require further, more detailed, studies. The electric properties of the material after proton irradiation can be completely restored at $T = 800^\circ\text{C}$.

1. Introduction

Among various kinds of particles used in studies of defects in irradiated Si such as MeV electrons and protons as well as neutrons, proton bombardments occupy the next place after fast electrons. The reasons are obvious. In contrast to fast neutron irradiation of Si mostly producing such extended defects as disordered regions, proton irradiation of Si is known to introduce point defects for the most part, especially in the range of energy loss by ionization effects. At the end of their range being characteristic of Non-Ionization Loss Energy (NIEL) the protons effectively create a lot of defects. In addition, their presence in this region makes it possible to investigate passivation effects by hydrogen.

It has long been known that there are many defects produced in Si by protons at energies of a few hundreds of keV to few MeV, being very similar to those produced by fast electrons; see for instance review papers [1,2]. As compared to fast electron irradiation, proton irradiation of Si makes it possible to produce intrinsic defects like vacancies V and self-interstitials Si_i at rates larger by several orders of magnitude. Because of this, the doses of proton irradiation at MeV energies used in defect studies are relatively low, from a few 10^{10} to a few 10^{12} protons/cm². Much heavier doses, $\Phi \geq 10^{15}$ protons/cm², are applied to degenerate materials as well as in some specific experimental techniques, e.g. positron annihilation experiments. Lower excitation of the electronic subsystem of the Si lattice during irradiation is another peculiarity of proton irradiation as compared to conditions of electron irradiation.

It should be noted that radiation effects of proton irradiation of Si over an energy interval between $E \approx 10$ MeV and $E \approx 100$ MeV are scarcely investigated; see for instance review paper [3]. The information on radiation-produced defects furnished by studies for lesser energy of protons, $E \leq 2$ MeV, has been thought to be relevant to irradiation of Si with protons at much higher energies, too. Partial evidence for this has been cited in experiments on Si irradiated with 24 GeV/c protons [4]. At the same time, however, there is ample evidence that some distinctions of defect interactions in floating-zone *n*-Si irradiated with 8 and 15 MeV protons are making their appearance [5]. The aims of the present work is to get a deeper insight into the problem.

2. Experimental

In this work we used the same *n*-Si crystal grown by the floating-zone (FZ) technique as that material studied in earlier investigations on radiation defects produced by electron irradiation [6]. The single crystal was doped with phosphorus at a doping level of $5 \cdot 10^{15}$ to $7 \cdot 10^{15}$ cm⁻³. The concentrations of residual oxygen and carbon were less than $3 \cdot 10^{16}$ and $7 \cdot 10^{15}$ cm⁻³, respectively. Square-shaped samples were cut from wafers of 0.4 or 0.9 mm thick.

Electrical measurements of charge carrier concentration and mobility, $n(1/T)$ and $\mu_e(T)$, respectively, were carried out in the Van der Pauw geometry over a temperature range of $T \approx 20$ to 300 K. Analyses of $n(1/T)$ curves with the aid of relevant equations of charge balance furnish additional information on concentrations of electrically active centers in *n*-type material making use of the statistics of electrons

in a non-degenerate semiconductor; see for instance [6]. The method allows one to separately determine the total concentration N_D of shallow donor states with an ionization energy of ≈ 43 meV due to substitutional phosphorus atoms as well as the total concentration N_A of all compensating acceptors. It must be emphasized that the N_D values include the shallow donor states D^0 being neutral at $T = 0$ K and also those D^+ being empty of electrons owing to compensation by acceptor centers. Along with this, the N_A values include all concentrations of compensating acceptors whose energy levels lie below shallow donor states at $\approx E_C - 43$ meV, where E_C is the bottom of the conduction band. In other words, N_D and N_A provide a general look at the total concentrations of electrically active centers and their changes in material prior to and after irradiation as well as in the course of isochronal annealing. The annealing steps were $\Delta T = 20^\circ\text{C}$ and $\Delta t = 10$ min. The reference temperature during isochronal annealing was 20°C .

Samples were irradiated with a pulsed beam of protons at 8 and 15 MeV. The frequency of the pulsed beam was 100 cps and the duty cycle was 2.5 ms. To prevent heating the samples in the course of proton irradiation the average current was kept low, in an interval of 10 to 100 nA/cm². Under these conditions the irradiation temperature didn't exceed 20°C . The accuracy of radiation dosage was about 15 percent.

The range of 15 MeV protons in bulk Si was calculated by TRIM to be $1440\mu\text{m}$. Taking into account that the particle straggling is $60\mu\text{m}$ one can estimate that the concentration of hydrogen at a distance about $900\mu\text{m}$ shouldn't be $\leq 10^{10}\text{ cm}^{-3}$ at a dose of $\Phi = 8 \cdot 10^{13}$ protons/cm². This is an upper estimate for bulk Si. Therefore, most incident protons at 15 MeV left samples 0.4 mm and 0.9 mm thick without noticeable effects of passivation.

In the case of 8 MeV protons their range in bulk Si was calculated to be $480\mu\text{m}$. The particle straggling is $22\mu\text{m}$, so the hydrogen concentration at a distance about $416\mu\text{m}$ shouldn't exceed $1 \cdot 10^{14}\text{ cm}^{-3}$ at a dose of $\Phi = 4 \cdot 10^{13}$ protons/cm². Anyway, a passivation effect possible in a thin layer of the surface couldn't markedly affect electrical measurements in the bulk of a sample 0.4 mm thick.

The last point concerns excitation conditions of the electronic subsystem of the Si lattice during proton and electron irradiation. Our estimates showed that the generation rate of electron-hole pairs was $G_{e-h} \approx 7 \cdot 10^{19}\text{ cm}^{-3} \cdot \text{s}^{-1}$ for the 15 MeV proton irradiation if the energy for creation of an electron-hole pair in Si is taken as 3.6 eV. This should be compared to $G_{e-h} \approx 7 \cdot 10^{20}\text{ cm}^{-3} \cdot \text{s}^{-1}$ for the 0.9 MeV electron irradiation in [6].

3. Results and Discussion

3.1. Initial material

The electrical parameters of $n\text{-Si(FZ)}$ samples prior to irradiation were good. The compensation ratio $K = N_A/N_D$

was very low, $K \leq 0.01$, and the charge carrier mobility at $T \approx 20$ K was $\mu_e \approx 3 \cdot 10^4\text{ cm}^2/\text{V} \cdot \text{s}$.

3.2. Proton irradiation of $n\text{-Si(FZ)}$

As is seen in Fig. 1 and 2, the concentration of charge carriers in $n\text{-Si(FZ)}$ irradiated with MeV protons decreases rapidly with increasing dose. At early stages of irradiation the removal rates of charge carriers are (210 ± 20) and $(110 \pm 20)\text{ cm}^{-1}$ for the 8 and 15 MeV protons, respectively.

To have a deeper look at formation processes of radiation defects we analyzed some $n(1/T)$ curves taken on the proton-irradiated samples; Fig. 1 and 2. The concentrations N_{DKF} and N_A calculated in the fitting procedure are given in Fig. 3. It is clearly seen that at each dose Φ the changes $\Delta N_D = N_D^0 - N_D(\Phi)$ are by a factor of $\sim 3-4$ larger than the changes $\Delta N_A = N_A(\Phi) - N_A^0$ where N_D^0 and N_A^0 are the concentrations of shallow donors and compensating acceptors prior to irradiation, respectively. This effect is much more pronounced for the 8 MeV proton irradiation. It means that radiation acceptors are produced at a much slower rate than the rate of loss of shallow donor states due to interactions between substitutional phosphorus atoms and intrinsic defects, i.e. mobile vacancies V and self-interstitials Si_i . In other words, the dominant phosphorus-related defects appear to be electrically neutral in n -type material, e.g. they may be deep donors. Surprisingly, such well-known radiation acceptors like vacancy-donor

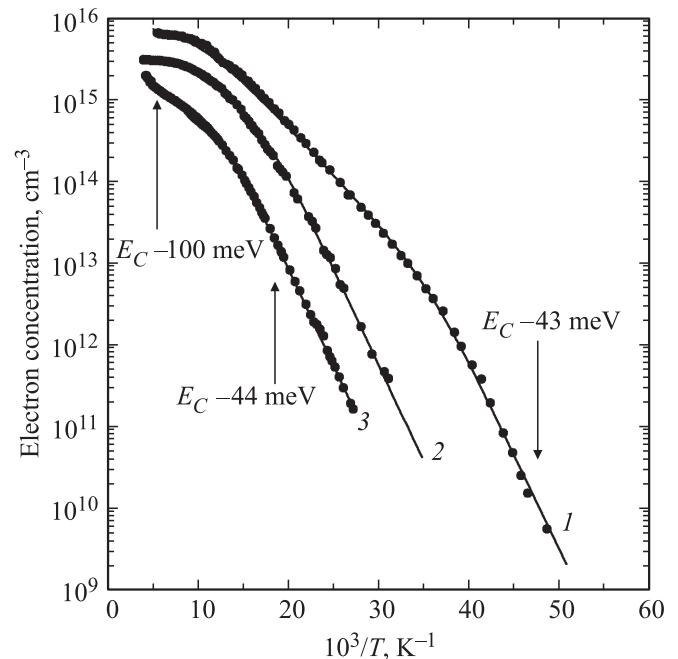


Figure 1. Electron concentration against reciprocal temperature for the $n\text{-Si(FZ)}$ sample irradiated with 8 MeV protons. Dose, protons/cm²: 1 — 0, 2 — $3 \cdot 10^{13}$, 3 — $5 \cdot 10^{13}$. Points, experimental; curves, calculated. Ionization energies of shallow donors and radiation defects are indicated.

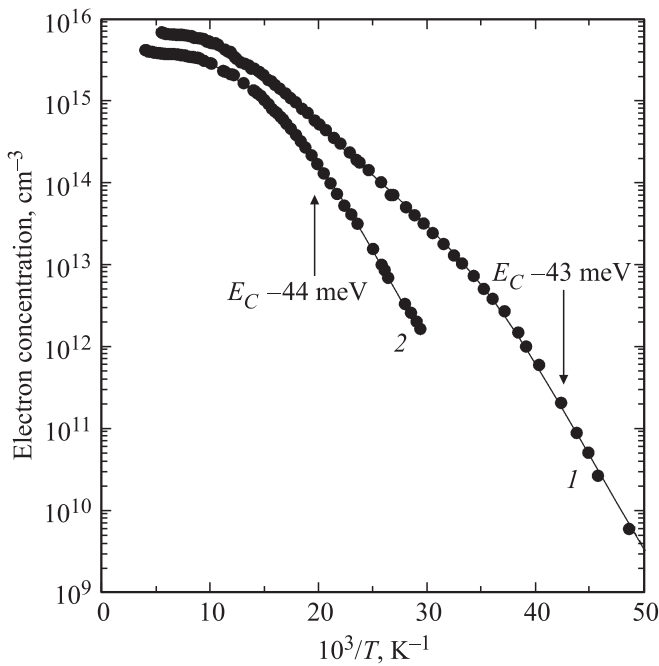


Figure 2. Electron concentration against reciprocal temperature for the *n*-Si(FZ) sample irradiated with 15 MeV protons. Dose, protons/cm²: 1 — 0, 2 — $4 \cdot 10^{13}$. Points, experimental; curves, calculated. Ionization energy of shallow donors is indicated.

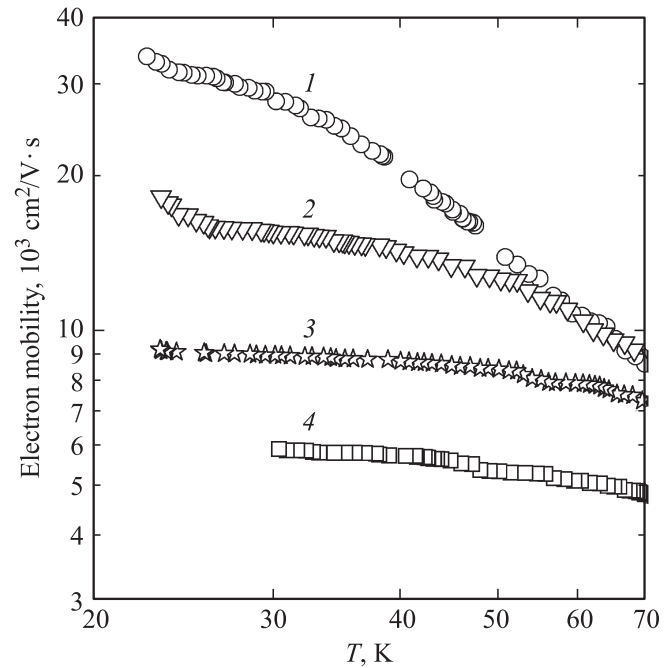


Figure 4. Electron mobility against temperature for the *n*-Si(FZ) sample irradiated with 15 MeV protons. Dose, protons/cm²: 1 — 0, 2 — $2 \cdot 10^{13}$, 3 — $3 \cdot 10^{13}$, 4 — $4 \cdot 10^{13}$.

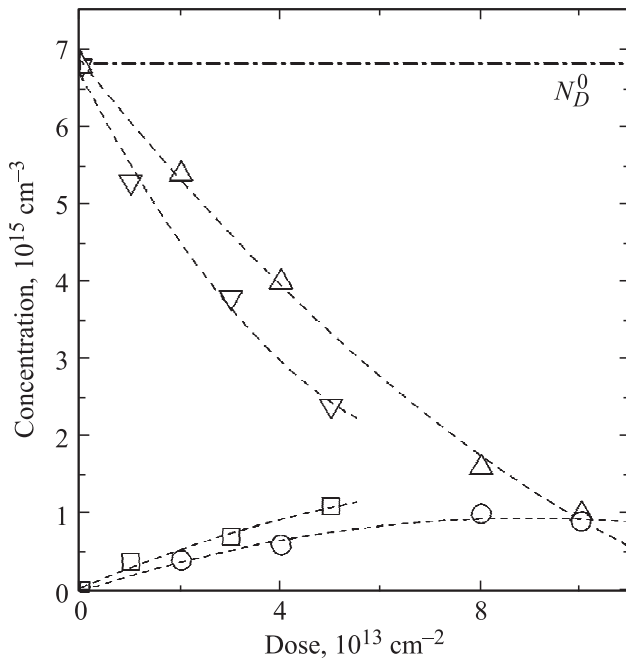


Figure 3. Total concentrations of shallow donors and deep acceptors against dose of proton irradiation at 8 and 15 MeV. Total concentrations of shallow donors N_D are given for proton irradiation at 8 MeV (triangles down) and 15 MeV (triangles up). Total concentrations of deep acceptors N_A are given for proton irradiation at 8 MeV (squares) and 15 MeV (circles). The initial concentration of shallow donors N_D^0 is also shown. Curves are the eye guides.

pairs $[VP_s]$ (*E*-centers) and divacancies V_2 play a minor part, in sharp contrast to what is widely believed in the literature for a long time. In Fig. 3 it is also seen that the formation kinetics of N_A levels off at heavier doses. In addition, in the *n*-Si(FZ) irradiated at $\Phi \leq 4 \cdot 10^{13} \text{ cm}^{-2}$ the presence of electrically active radiation defects with ionization energies lower than 200 meV was not detected, within the accuracy of electrical measurements, about 10 percent; i.e. they may be introduced in concentrations $\leq 2 \cdot 10^{14} \text{ cm}^{-3}$. However, at heavier doses of $\Phi > 5 \cdot 10^{13} \text{ cm}^{-2}$ radiation defects at $\approx E_C - 0.1 \text{ eV}$ made their appearance, whose concentration could be only roughly assessed at $\leq 1 \cdot 10^{15} \text{ cm}^{-3}$ in samples following 15 MeV proton bombardment at $\Phi = 1 \cdot 10^{14} \text{ cm}^{-2}$. Comparing their concentration and the total concentration of all radiation-produced acceptors $N_A \approx 1 \cdot 10^{15} \text{ cm}^{-3}$ one may conclude that these defects are of donor type.

Let us turn now to the mobility of charge carriers in proton-irradiated *n*-Si(FZ). Irradiations of the *n*-Si(FZ) with protons at 8 and 15 MeV do produce a profound effect on the concentration and mobility of charge carriers in *n*-Si(FZ). As an illustration, Fig. 4 displays a dramatic drop of the mobility μ_e , especially at $T \leq 100 \text{ K}$. Moreover, the shape of $\mu_e(T)$ curves demonstrates a very weak temperature dependence at $T \leq 70 \text{ K}$ like in SiGe alloys [7]. Despite the presence of ionized centers in considerable concentrations, the $\mu_e(T)$ curves at low cryogenic temperatures, $T \leq 40 \text{ K}$, do not feature any behavior being characteristic of the scattering by ionized centers, $\mu_e \propto T^{3/2}$; see for instance [8].

3.3. Comparison to fast electron irradiation of *n*-Si(FZ)

The same material was earlier irradiated with electrons at 0.9 MeV and studied [6]. The removal rate of charge carriers was found to be 0.2 cm^{-1} . It was shown that the charge carrier concentration in electron-irradiated *n*-Si(FZ) is primarily decreased due to formation of vacancy-donor pairs when mobile vacancies produced by fast electrons are trapped by substitutional phosphorus atoms to form *E*-centers, which are single acceptors at $\approx E_C - 0.4 \text{ eV}$ [9]. If their formation plays the leading role among other vacancy-related defects, a 1:1 correspondence appears as $|-N_D| \approx +N_A$, where $|-N_D|$ is the loss of shallow donor states of substitutional phosphorus atoms and $+N_A$ is the increase in the concentration of radiation-produced acceptors. Careful electrical measurements on the electron-irradiated *n*-Si(FZ) have borne out this relationship [6]. Besides the dominant *E*-centers which act in electron-irradiated *n*-Si(FZ) as deep compensating acceptors, other radiation defects whose energy states are above $\approx E_C - 0.2 \text{ eV}$ could be present only in small concentrations $\leq 2 \cdot 10^{14} \text{ cm}^{-3}$, similar to the case here of *n*-Si(FZ) irradiated with protons at $\Phi \leq 4 \cdot 10^{13} \text{ cm}^{-2}$. As opposed to MeV proton irradiation, a possible contribution of divacancies V_2 as compensation effects in *n*-Si(FZ) following 0.9 MeV electron irradiation is expected to be very low, since their production rate is less than 0.003 cm^{-1} [10]; compared to the *E*-center formation rate being equal to 0.11 cm^{-1} [6]. Along with this, radiation defects at $\approx E_C - 0.1 \text{ eV}$ observed here in the proton-irradiated *n*-Si(FZ) are lacking in the electron-irradiated samples. Despite a seemingly simple formation of radiation defects in electron-irradiated *n*-Si(FZ) the annealing processes display complexity. They will be discussed in detail in a separate paper.

It is worth noting that a dramatic impact of proton- and electron irradiation on the charge carrier mobility in the same *n*-Si(FZ) can be characterized in a similar way; see also [6]. Low values of the mobility at $T \leq 70 \text{ K}$, together with a very weak temperature dependence, invite us to suggest that the effect stems from the presence of radiation-produced defects giving rise to large elastic deformations in the crystal lattice. The mobility behavior in strongly diluted $\text{Si}_{1-x}\text{Ge}_x$ alloys [7] gives one a broad hint to a new component in the charge carrier scattering. There are some indications that the elastic deformations associated with radiation defects, most likely being of interstitial type in irradiated *n*-Si(FZ), are non-uniform. Additional experiments on detecting orientation-sensitive effects are now in progress.

3.4. Defect annealing processes in proton-irradiated *n*-Si(FZ)

Fig. 5 displays the recovery of the free carrier concentration at 25°C of proton-irradiated *n*-Si(FZ) upon isochronal annealing. As is seen, the annealing behavior appears

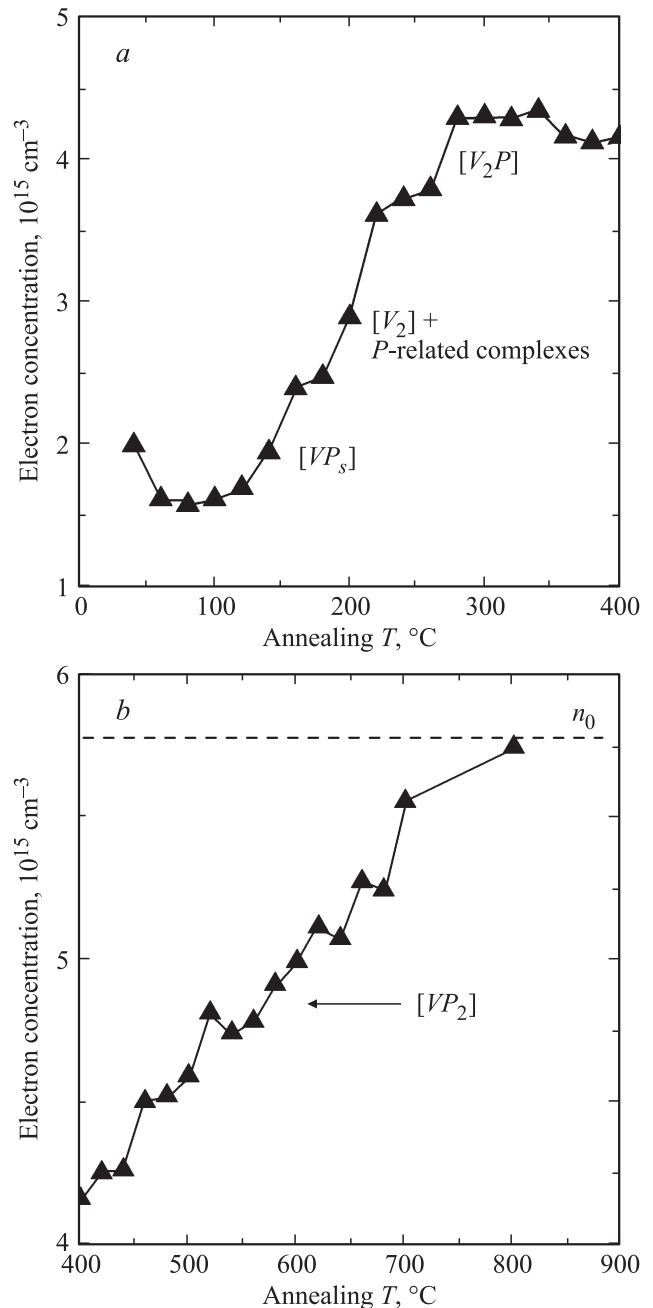


Figure 5. Recovery stages of the charge carrier concentration for one of the *n*-Si(FZ) samples subjected to 15 MeV proton irradiation and subsequent isochronal annealing at $T \geq 400^\circ\text{C}$ (a) and $T \geq 400^\circ\text{C}$ (b). Dose, $6 \cdot 10^{13} \text{ protons/cm}^2$. The proposed identification of several annealing stages is given; see also text.

to be rather complicated, revealing many stages of the recovery with the increasing temperature, up to $T \approx 800^\circ\text{C}$. This complexity is obviously related to high concentration of phosphorus atoms in irradiated samples, on one hand, and heavy irradiation dose, on the other hand. In actual fact, most papers devoted to electrical measurements on proton-irradiated *n*-Si, among them conductivity, Hall effect, and DLTS, are concerned with lightly doped materials

and low doses of proton irradiation at $E \leq 2$ MeV and $10^{11} \leq \Phi < 10^{13} \text{ cm}^{-2}$. As a result, the radiation-produced defects have usually disappeared at $T \leq 400^\circ\text{C}$. Because of this, the annealing curves in Fig. 5 are divided into two temperature intervals, $T \leq 400^\circ\text{C}$ and $T \geq 400^\circ\text{C}$. Electrically active defects being known to anneal at a specific stage are indicated based on relevant information gained by means of other techniques such as EPR, IR spectroscopy, DLTS, positron annihilation, etc. Included also are processes to be suggested upon further analysis here. In the present paper the annealing behavior is discussed in general terms, based solely on the restoration processes of charge carrier concentration. A detailed comparison of defect annealing in the electron- and proton-irradiated *n*-Si(FZ), including some recovery stages of shallow donors, will be given in a separate paper.

Fig. 5, *a* shows that some changes in defect concentrations are observed even at $T \approx 40^\circ\text{C}$, giving rise to a negative annealing stage. Then the well-known annealing stage of *E*-centers makes its appearance at $100 \leq T \leq 200^\circ\text{C}$; see for instance [9]. In this way, an estimate of the production rate of $[VP_s]$ pairs can be assessed, $\sim 6 \text{ cm}^{-1}$. In the case of 0.9 MeV electron irradiation of the same material the *E*-center production rate was found to be 0.11 cm^{-1} . As we shall see subsequently, a partial annealing process of *E*-centers will be interpreted to occur via their diffusion to substitutional phosphorus atoms P_s^+ resulting in the formation of vacancy-two phosphorus atom complexes $[VP_2]$.

It should also be noted that at this annealing stage the concentration of radiation defects with an ionization energy $\sim 100 \text{ meV}$ is strongly decreased, so that after the annealing step at $T \approx 100^\circ\text{C}$ their presence is scarcely detectable.

The next annealing stage at $200 \leq T \leq 280^\circ\text{C}$ is known to be associated with divacancies V_2 [11,12]. Actually, their diffusivity in this temperature interval, a few $10^{-15} \text{ cm}^2/\text{s}$, makes it possible to move them through the crystal at a distance of a few hundred Å; see for instance [12]. A clearly defined stage of $T = 220$ to 280°C being attended by a substantial recovery of the charge carrier concentration in 10 MeV proton-irradiated *n*-Si(FZ) was earlier reported in [13]. An important point is that this annealing stage was accompanied with a pronounced disappearance of an IR band at $3.3 \mu\text{m}$. Among other IR bands associated with divacancies [14], the $3.3 \mu\text{m}$ band is known to be characteristic of V_2^{2-} in Si. In our case the charge state of divacancies is concluded to be V_2^- taking into account the Fermi level position at $\approx E_C - 0.43 \text{ eV}$ in the temperature interval indicated above. The deep acceptor state of divacancies (V_2^-/V_2^0) is reportedly to be placed at $E_C - 0.42(4) \text{ eV}$ [11]. Therefore, the fraction of V_2^- during the anneal should be about one half. The Fermi level at the reference measurement point of $T = 290 \text{ K}$ is shifted up to $\approx E_C - 0.24 \text{ eV}$, close to the upper acceptor states of (V_2^{2-}/V_2^-) lying at $E_C - 0.23(9) \text{ eV}$ [11]. Therefore, an upper limit of the concentration of V_2 could be set at $N \leq 5 \cdot 10^{14} \text{ cm}^{-3}$ at $\Phi = 6 \cdot 10^{13} \text{ cm}^{-2}$. However, this is certainly an oversized estimate taking into account that

a partial recovery of shallow donors, about $7 \cdot 10^{14} \text{ cm}^{-3}$, was revealed in the same temperature interval. Earlier the contributions of *E*-centers and divacancies in 10 MeV proton-irradiated *n*-Si(FZ) at the relevant annealing stages were concluded to be equal at $\Phi = 5.1 \cdot 10^{12} \text{ cm}^{-2}$ [13], but the authors discussed the annealing stage of divacancies only as the disappearance of compensating acceptors, without any contribution of an annealing process of phosphorus-related defects. The equal contributions of $[VP_s]$ pairs and divacancies seem to be unexpected, since the production rate of isolated vacancies should be much higher than that of divacancies. This issue will be discussed elsewhere, together with the annealing behavior of radiation defects in the same electron-irradiated *n*-Si(FZ) after 0.9 MeV electron irradiation.

The third stage of defect annealing occurs over a temperature interval of $T = 250$ to 280°C ; see Fig. 5, *a*. It could be ascribed to annealing of vacancy-oxygen pairs $[VO]$, being labelled the *A*-centers [15]. In earlier experiments with the use of electrical measurements on proton-irradiated *n*-Si this annealing stage was generally attributed to *A*-centers; see for instance [13]. However, in our case it is hardly conceivable that the concentration of *E*-centers in the irradiated *n*-Si(FZ) could be equal to the concentration of *A*-centers, taking into account the interactions between mobile vacancies V^- or V^{2-} and substitutional phosphorus atoms P_s^+ , on one hand, and electrically inactive oxygen atoms, on the other, provided the concentrations of impurity atoms are of the same order of magnitude.

Furthermore, there is additional useful information furnished in positron annihilation experiments on vacancy-type defects in irradiated oxygen-rich *n*-Si that substantiates this statement. First of all, the lifetime of positrons in irradiated *n*-Si containing *A*-centers was found to be $\tau_A \approx 225 \text{ ps}$ [16,17]. Because of a specific atomic structure of *A*-centers this differs little from the lifetime of positrons in initial material, $\tau_0 \approx 217 \text{ ps}$. Actually, it is known that the vacancy-oxygen complex can be visualized as a substitutional oxygen atom in a slight off-center position [15], thus reducing the open volume of the vacancy. Together with this, recent positron annihilation experiments on the same *n*-Si(FZ) following 15 MeV proton irradiation [18] revealed that new positron-sensitive defects are formed at these temperatures. They are concluded to be of vacancy-type, for the lifetime of positrons trapped by these defects proved to be about $\tau \approx 276 \text{ ps}$. Actually, it should be compared to the calculated positron lifetime for the (unrelaxed) single vacancy in Si, $\tau = 254$ to 261 ps and the positron lifetime for the divacancy $\tau \approx 300 \text{ ps}$, extracted from positron annihilation experiments on electron- and proton-irradiated Si; see [19] and the literature therein. It should be noted that in the initial *n*-Si(FZ) τ was equal to 216 ps . A decrease in the positron lifetime for the defect considered by ten percent in respect to $\tau \approx 300 \text{ ps}$ for the isolated divacancy is thought to be due to a reduction in the open volume of the divacancy-related defect by a trapped atom whose involvement in the complex retaining both

vacancies as the constituents. Reasoning from this knowledge we suggest that negatively charged divacancies, being mobile at $T \geq 200^\circ\text{C}$, can be trapped by substitutional phosphorus atoms P_s^+ giving rise to divacancy-impurity complexes $[V_2P]$. This trapping reaction is thought to be realized. As is indicated above, the fraction of divacancies V_2^- at the annealing stage of $T \approx 220$ to 280°C should be sizable, nearly one half. Consequently, their trapping should be enhanced by the Coulomb attraction. Taking into consideration the diffusion length for V_2 , the Debye radius and concentrations of charged defects our estimates showed that a marked fraction of divacancies may be involved in the trapping process. Strong support to our consideration can be found in radiation experiments on oxygen-enriched n -Si subjected to electron irradiation [11,12,19]. It should be remarked that a phosphorus atom in this divacancy-impurity complex may be placed between two vacancies $[VPV]$ or at the end of the divacancy $[PVV]$.

These complexes $[V_2P]$ were found to be stable up to $T \approx 400^\circ\text{C}$. They can be annealed out at $T \approx 450$ to 470°C and after this annealing stage the positron lifetime τ in the proton-irradiated n -Si(FZ) drops to its initial value about 216 ps. Interestingly, further inspection of Fig. 5, *a* tells us that the formation of $[V_2P]$ complexes at $T \approx 280^\circ\text{C}$ is accompanied with a pronounced increase in the charge carrier concentration. By an example, this may occur if radiation defects being double acceptors are transformed into other defects having single acceptor states.

Among other high-temperature annealing stages of radiation defects, special attention must be drawn to a remarkable stage of defect annealing between $T \approx 570$ to 650°C . It should be pointed out that this stage is also observed in the same n -Si(FZ) subjected to 0.9 MeV electron irradiation. In this case the divacancy production is very small and, thus, the picture of defect annealing becomes more clear. Particularly, our electrical measurements demonstrated that the annealing of each radiation acceptor in this temperature interval is accompanied by restoration of two shallow donors. Because of this, a model of vacancy-two impurity atoms complexes $[VP_2]$ is put forward. Their formation at the annealing stage of E -centers can be visualized as a trapping process of mobile vacancy-phosphorus atom pairs by isolated substitutional phosphorus atoms, being enhanced by the Coulomb attraction of $[VP_s]^-$ to P_s^+ . Earlier EPR measurements on strongly doped n -Si subjected to electron irradiation revealed the presence of radiation defects which could be identified as such complexes in the $[P_sVP_s]$ configuration [20]. Theoretical treatment of such complexes allows one to conclude that the complexes under consideration should be electrically active as single acceptors in Si [21].

In conclusion of this section, let us touch on the question of how the charge carrier mobility in proton-irradiated n -Si(FZ) is restored upon annealing; see Fig. 6. Of great importance is the fact that the mobility can be totally restored in the course of annealing, up to initial values. In this way it has been demonstrated that

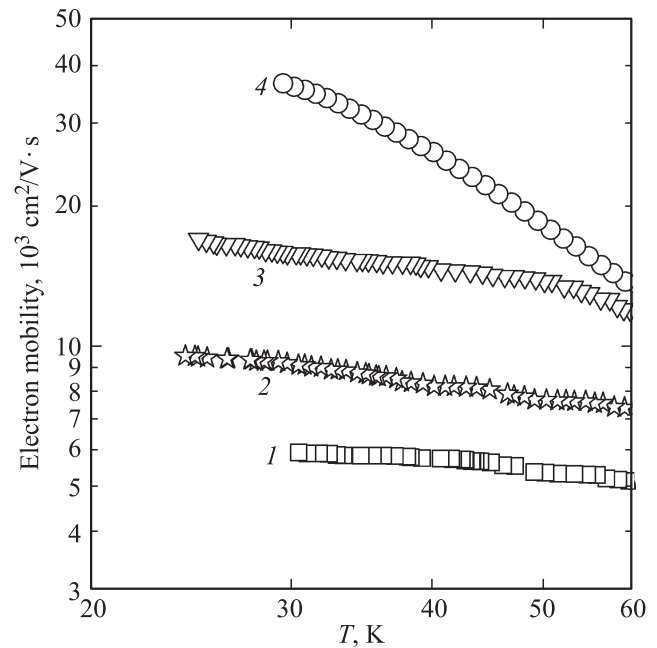


Figure 6. Electron mobility against temperature for the n -Si(FZ) irradiated with 15 MeV protons. Dose, protons/cm²: $4 \cdot 10^{13}$. Annealing temperature, $^\circ\text{C}$: 1 — irradiated, 2 — 200, 3 — 500, 4 — 800.

the striking changes of the mobility in the course of irradiation and annealing are closely related to radiation defects. After a final step of annealing at $T = 800^\circ\text{C}$, our analysis of $n(1/T)$ curves provided conclusive evidence that the electron concentration was completely recovered, too. Surprisingly, it turned out that the compensation ratio of electron conductivity in the annealed samples proved to be very small, $K = N_A/N_D \leq 0.01$, just as prior to the irradiation.

4. Conclusions

Electrical properties of radiation defects in n -Si(FZ) subjected to 8 and 15 MeV proton irradiation were studied with the help of Hall effect measurements over a temperature range of $T \approx 25$ to 300 K. Analysis of electrical data allowed us to get a deeper insight into formation and annealing processes of radiation defects. Together with such well-known defects like vacancy-donor pairs and divacancies, some new vacancy-related complexes were found, among them such complex defects proposed to contain a divacancy tied with a phosphorus atom and a vacancy tied with two substitutional phosphorus atoms. Also observed were new phosphorus-related defects being distinctly different from what has already been known for the various vacancy-type complexes with the involvement of phosphorus impurity atoms. Importantly, these new defects were found to be electrically neutral in n -Si(FZ). It was revealed that at the beginning of proton irradiation they are produced at a much higher rate than radiation defects of acceptor type. So far,

our results reveal no information concerning their identity and little information concerning their specific role in the carrier concentration annealing recovery processes. This intriguing question invites further extensive investigation. In particular, it requires more detailed $n(T)$ information concerning the annealing processes in a temperature range of $T \approx 100$ to 300°C where $[VP_s]$ pairs and divacancies disappear, to separate out better the individual defect contributions, see for instance [22]. DLTS studies would be particularly helpful. A predominance of electrically neutral defects containing phosphorus impurity atoms over those of acceptor type may mean that there could be some kinds of electrically neutral complexes with the involvement of vacancies also, taking into consideration the creation of self-interstitials and vacancies in equal concentration. This brings up another point. At present it is not clear why irradiation of *n*-Si(FZ) with energetic protons can strongly change the reaction paths of defects as opposed to fast electron irradiation.

Another principal issue is the nature of a new defect-related component that exerts a dramatic impact on the charge carrier scattering in irradiated *n*-Si(FZ). Surprisingly, there are many similarities in the mobility behavior under electron- and proton-irradiation, most likely associated with self-interstitials.

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