TWO MECHANISMS OF ANNEALING OF DIVACANCIES IN IRRADIATED n-Si CRYSTALS

T.A. PAGAVA, N.T. BZHALAVA, N.I. MAISURADZE, D.Z. KHOCHOLAVA, L.S. CHKHARTISHVILI

Georgian Technical University, Department of Physics
(77, Kostava Str., Tbilisi 0175, Georgia; e-mail: tpagava@gtu.ge)

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We studied n-silicon samples obtained by the floating-zone method and irradiated by 2-MeV electrons with a majority-carrier concentration of 6×10^{13} cm^{-3}. It is shown that, in irradiated n-Si samples, divacancies are annealed by means of two mechanisms: their conversion to other complexes (V_2O or PV_2) or dissociation into separate monovacancies.

1. Introduction

The most extensively studied multivacancy complexes in silicon are divacancies (DV, V_2). They can be formed by two mechanisms: 1) if an incident particle transfers the energy sufficient for a shift of two neighboring silicon atoms to a crystal, then a DV can be formed as a primary defect; 2) if the electron energy is equal to 1.5 eV, then the rate of DV introduction amounts to 5% of the rate of vacancy formation. It is worth noting that the measurements were performed at a temperature of the crystals equal to 20 K. The following heating of the crystals resulted in the vanishing of the isolated vacancy spectrum and the growth of the DV number in the crystals with low oxygen concentration. In the given case (i.e. at low radiation energies), the diffusion mechanism of DV formation prevails over the cascade one [1, 2]. As is known, the irradiation of silicon crystals by high-energy particles gives rise to the generation of amorphous inclusions in them. The molecular-dynamics simulation shows [3] that these inclusions can also serve as effective sources of point structural defects and, in particular, divacancies due to their higher stability as compared to the inclusions themselves.

Due to the calculations performed in [4], the structures and energy characteristics of the simple and split divacancies in silicon are currently known. The energies of their formation are estimated as 4.63 and 5.90 eV, respectively. In any case, the DV binding energy approximates 2 eV.

DVs exist in various charge states [5]: V_2^+, V_2^0, V_2^-, and $V_2^{=}$. In particular, it was established in [6] that the main radiation-induced defect in phosphorus-doped n-Si (along with E-centers, i.e. $V+P$ pairs) is a doubly charged negative divacancy. Divacancies can exist in silicon in several states that differ in the induced lattice distortion. It was shown [7] that the DV electron levels measured experimentally at common temperatures do not appear due to these states; instead, they correspond to some state averaged over the atomic motion (electron levels at certain distortions can be measured only at very low temperatures, at which the divacancy in one of them is “frozen out”). The form of the silicon lattice distortion induced by a doubly charged negative divacancy was proposed in [8]. According to theoretical researches [9], the presence of a neutral divacancy at room temperature gives rise to such a distortion in a silicon lattice that the system oscillates between two states weakly differing in energy (by $\sim$10 meV).

The possible charge states of divacancies in silicon were studied theoretically in [10]. These investigations yielded the energies of their formation, as well as the binding and ionization energies. The study of their atomic and electron structures results in the conclusion [11] that the charge states of a divacancy cause a larger distortion. Such characteristics as the atomic configuration, the energies of formation and electron transitions, and the binding energy for these charge states were calculated in [12] (see also [13]). It was established that the ground-state configuration depends on the charge state of a divacancy.

As is known [4, 5], divacancies in silicon are annealed due to their diffusion in the lattice until they are captured by a trap. Moreover, they can diffuse in the lattice over large distances without dissociation, because the activation energy of divacancy diffusion is approximately equal to 1.25 eV, while the energy of its dissociation is close to 2 eV. Divacancies effectively interact with impurity I atoms with the formation of

$V_2 + \mathrm{I}$ complexes. For example, the effective formation of V_2O, V_2O$_2$, HV_2, SnV_2, Sn$_2V_2$, GeV_2, and other complexes takes place [5, 14, 15].

Our investigations demonstrated that the annealing of DVs in boron-doped p-Si crystals irradiated by 8-MeV electrons takes place by means of their conversion into BV_2 complexes [16–18]. This complex was already calculated theoretically [19]. According to these calculations, the binding energy between a divacancy and a boron atom at a site appeared close to 0.2 eV. As for the electron levels of the BV_2 complex, they must lie close to the corresponding levels of a free divacancy. It was noted that this complex and the mechanism of divacancy annealing with the formation of BV_2 will play a very important role only in silicon heavily doped with boron.

In n-Si crystals with the oxygen concentration $N_{\mathrm{O}} \approx 2 \times 10^{16}$ cm^{-3}, divacancies are annealed by means of their conversion to V_2O complexes [20] (the possibility of identification of the products of the DV annealing with V_2O in silicon specially oxidized up to $N_{\mathrm{O}} \sim 10^{17}$ cm^{-3} was discussed in [21]). In samples with the oxygen concentration $N_{\mathrm{O}} \approx 5 \times 10^{15}$ cm^{-3}, divacancies are annealed due to their dissociation into separate monovacancies, which results in the negative annealing of A-centers. The observed effect (dissociation of a certain part of divacancies) was explained in [20] as a result of the low concentration of oxygen atoms ($N_{\mathrm{O}} \approx 5 \times 10^{15}$ cm^{-3}) and, respectively, the small number of A-centers formed under irradiation as compared to the number of DVs. The authors of work [22] also ascribed the negative annealing of A-centers in the range 230–300 °C in the process of isochronous annealing (IA) to the DV dissociation. It is worth noting that the negative annealing of A-centers can be observed in the cases where the dominant mechanism of DV annealing is the formation of V$_2$O complexes. The matter is that the indicated complexes are, in turn, annealed by means of the dissociation into A-centers (i.e. V+O-complexes) and monovacancies: $V_2\mathrm{O} \rightarrow \ A \ + \ V$ [23, 24]. The migration energy of a divacancy before it gets to a trap represented by interstitial oxygen is estimated as 1.3 eV [23], whereas the process of interaction of a divacancy with oxygen is characterized by the activation energy equal to 2.02 ± 0.12 eV [24] and runs under the annealing in the temperature interval 275–355 °C. After that, the generated A-centers can migrate to interstitial oxygen atoms, by forming VO$_2$ complexes or (in the case of a long-term annealing) VOH and VOH$_2$ complexes with hydrogen atoms that can move, in turn, in the silicon lattice.

The aim of this work is to establish the annealing mechanism (conversion or dissociation) of divacancies in n-Si crystals irradiated at various temperatures.

2. Experimental Technique

We studied n-silicon samples grown by the floating-zone method with the majority-carrier concentration equal to 6×10^{13} cm^{-3}. The oxygen concentration determined by the infrared absorption amounted to $\sim 2 \times 10^{16}$ cm^{-3}, whereas the density of growth dislocations obtained from etching pits did not exceed 4×10^4 cm^{-2}. The samples were cut off in the form of slugs 1×3×10 mm in size with the largest face (111). One part of the studied samples was irradiated by 2-MeV electron pulses. The electron flux density $\varphi = 5 \times 10^{12}$ cm^{-2}·s^{-1}. The samples were irradiated at temperatures of 300 K and 473 K.

The second part of the samples was irradiated by protons with an energy of 25 MeV. The irradiation was performed in the pulsed mode. The pulse duration and the repetition rate were equal to 25 μs and 0.25 Hz, respectively. The proton flux density amounted to 1.5×10^{11} particles/cm^2 per pulse. The proton irradiation was performed at 300 K.

All the samples were irradiated along the direction normal to the largest face. The irradiation dose was chosen in such a way that the concentration of majority carriers captured by radiation-induced defects (RID) at 77 K did not exceed the concentration of the doping agent – phosphorus (N_P). In order to identify the defects appearing due to irradiation, we determined the ionization energy and the thermal stability of these centers.

The isochronous annealing of the studied samples was carried out in the temperature range 80–600 °C at a step of 10 °C. The time of keeping at a fixed temperature amounted to 10 min. After each IA cycle, the majority carrier concentration was measured using the Hall method between 77 and 300 K.

The ohmic contacts for measurements were created by rubbing aluminum into the surface of the studied samples.

The variation of the majority carrier concentration at 300 K was determined from the curves $N = f(10^3/T)$, where N is the electron concentration, and T is the absolute temperature. The ionization energies of the defect levels E_i were determined under the assumption that $\varepsilon_{\mathrm{F}} = E_i$, where ε_{F} is the Fermi level energy. In the case of n-Si crystals, we applied the formula

$$N = N_C F_{1/2}\left(\frac{\varepsilon_{\mathrm{F}}}{kT}\right),$$

where N_C is the effective state density in the valence band, $F_{1/2}$ is the Fermi–Dirac integral, and k is the Boltzmann constant. The corresponding regions of the dependences $N = f(10^3/T)$ were chosen with regard for the degree of depletion of a certain level. In strongly compensated samples, the energy E_i of different RIDs was determined from the slope of the dependences of the majority carrier concentration on the reciprocal temperature. The concentrations of various RIDs after each IA cycle were calculated with the help of the step dependences $N = f(10^3/T)$ and $N = f(T_{\rm ann})$ in the temperature ranges 77–300 K and 80–600 °C, respectively. As an example, Fig. 1 shows the electron concentration N as a function of the reciprocal temperature before the irradiation (curve *1*), after the electron irradiation with the dose $\Phi = 1.5 \times 10^{14}$ cm^{-2} at 300 K (curve *2*) and the isochronous annealing at 100 °C (curve *3*), 150 °C (curve *4*), and 300 °C (curve *5*). The concentration of A-centers N_A was determined with the help of curves *2–5* in Fig. 1: $N_A = N_{300} - N_{77}$. The concentration of E-centers N_E was measured from the variation of N at 300 K after the isochronous annealing in the interval 80–150 °C. As is known [1], the formation of E-centers in n-Si crystals with low oxygen content results in the removal of two electrons from the conduction band; therefore, $N_E = \Delta N/2$ (see curves *2* and *4*). It is known [2] that the energy level corresponding to doubly charged negative divacancies in the forbidden band is E_c-(0.21÷0.23) eV. Consequently, the divacancy carries one electron at 300 K, that is why the divacancy concentration N_{V_2} can be determined based on the change of N at 300 K after the isochronous annealing in the interval of annealing temperatures 150–300 °C, $N_{V_2} = \Delta N$ (see curves *4* and *5*). The further increase of $T_{\rm ann}$ also can provide information on the annealing kinetics of A-centers and more thermostable RIDs (not given in the figure). N_{300} denotes the electron concentration at T=300 K and N_{77} – at 77 K. The measurement error of these quantities did not exceed 10%.

3. Investigation Results and Their Discussion

As one can see from Fig. 2 (curve *1*), the concentration of A-centers in n-Si crystals irradiated at 300 K grows in the process of isochronous annealing in the range $T_{\rm ann}$ =80–150 °C, which is explained by the interaction of the vacancies released after the decay of E-centers with impurity oxygen atoms. Immediately after the irradiation, $N_A/N_{V_2} \approx 1$, where N_A and N_{V_2} are the concentrations of A-centers and V-centers, respectively. After the annealing at $T_{\rm ann}$=150 °C, $N_A/N_{V_2} \approx 2$, which

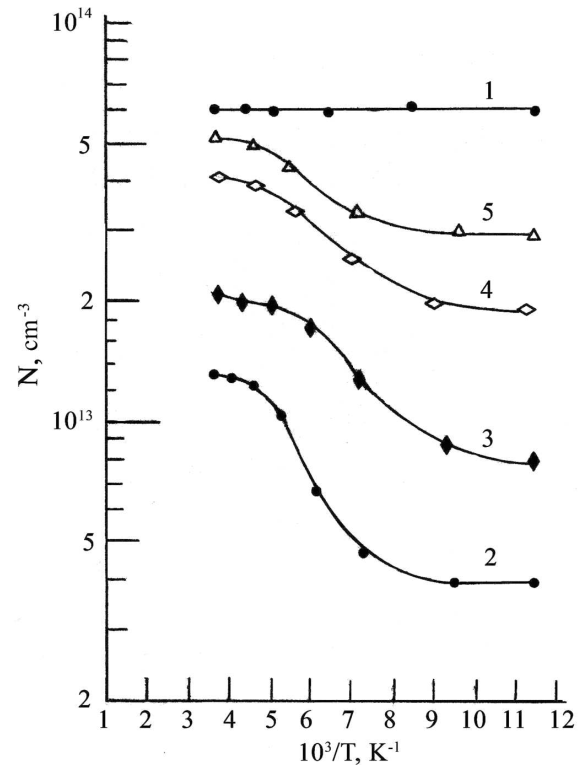

Fig. 1. Temperature dependences of the electron concentration in n-Si crystals before irradiation (*1*), after electron irradiation at 300 K ($\Phi = 1,5{\times}10^{14}$ cm^{-2}) (*2*), after annealing at $T_{\rm ann}$ = 100 °C (*3*), 150 °C (*4*), and 300 °C (*5*)

is caused by an increase of N_A due to the dissociation of E-centers. Under these conditions, the concentration of A-centers does not grow in the process of decay of divacancies in the interval 250–300 °C.

In order to get rid of the influence of E-centers, the studied samples were irradiated at a temperature of 200 °C. In the process of isochronous annealing, the concentrations of A-centers and divacancies in these crystals do not change up to $T_{\rm ann}$ = 250 °C, which is related to the absence of E-centers in the bulk of the crystal, that are completely annealed at $T_{\rm ann}$ = 150 °C and respectively cannot be generated at $T_{\rm ann}$ = 200 °C (Fig. 3). Under the radiation-induced increase of the crystal temperature from room one to 200 °C, the change of the efficiency η of introducing various RIDs in identical samples is mainly determined by three factors: the irradiation temperature, the concentration of nonequilibrium vacancies, and their charge state. The increase of $T_{\rm irr}$ results in the reduction of η; the vacancies released at $T_{\rm irr}$ = 200 °C due to the formation of E-centers give rise to the increase of η; the vacancy recharging with increase in $T_{\rm irr}$ leads to a growth of η as well. At 200 °C,

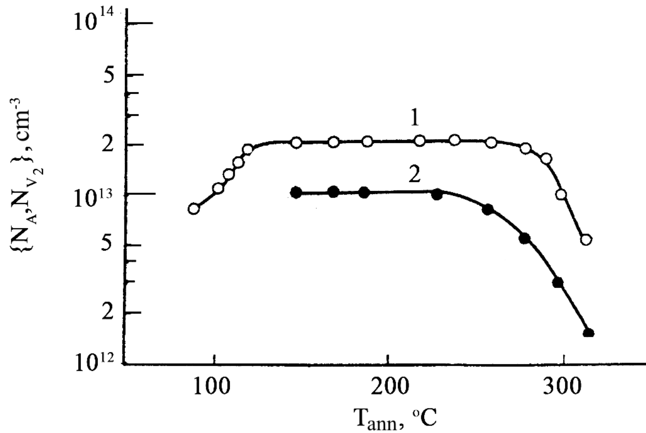

Fig. 2. Concentrations of A-centers (*1*) and divacancies (*2*) as functions of the IA temperature in n-Si samples irradiated by 2-MeV electrons. $T_{\rm ann}$ = 300 K, $\Phi_e = 1.5\times10^{14}$ cm^{-2}

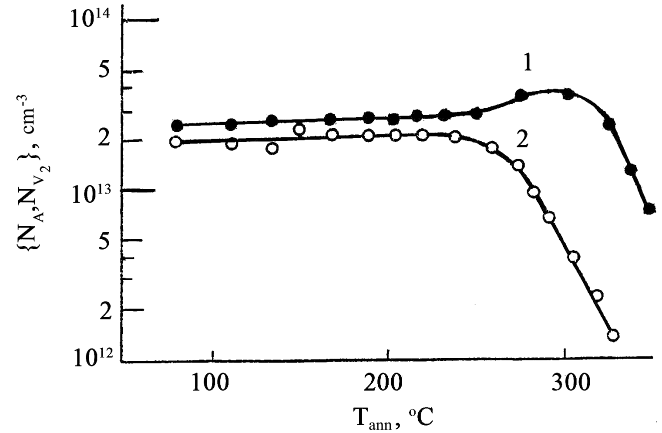

Fig. 3. Concentrations of A-centers (*1*) and divacancies (*2*) as functions of the IA temperature in n-Si samples irradiated by 2-MeV electrons. $T_{\rm ann}$ = 200 °C, $\Phi_e = 1.5\times10^{14}$ cm^{-2}

the studied samples with an electron concentration of 6×10^{13} cm^{-3} start manifesting intrinsic conductivity [25]. It is known [26] that, in the intrinsic conductivity region, vacancies exist in the neutral state, and, therefore, divacancies are generated not only as primary RIDs but also due to the diffusion mechanism, which increases η_{V_2}.

The combined effect of these three factors on the process of defect formation in n-Si samples irradiated at 200 °C results in the twofold decrease of the ratio N_A/N_{V_2}: $N_A/N_{V_2} \approx 1$ (Fig. 3, curves *1* and *2*).

In the samples irradiated at 300 K, $N_A = 0.9 \times 10^{13}$ cm^{-3}. In the process of isochronous annealing, N_A grows up to $N_A \approx 2.2 \times 10^{13}$ cm^{-3} (Fig. 2, curve *1*), which is caused by the dissociation of E-centers, as was already mentioned above. In the crystals irradiated at 200 °C, E-centers are not generated, and neutral vacancies released at $T_{\rm ann}$ = 200 °C due to the formation of E-centers cause a rise of both N_A and N_{V_2} (Fig. 3, curves *1* and *2*). That is why the ratio N_A/N_{V_2} almost does not change and remains the same as it was before the irradiation at $T_{\rm irr}$=300 K. The further increase of the annealing temperature results in a reduction of the DV concentration and the growth of the number of A-centers. Analyzing the experimental curves, one can see that the isochronous annealing results in the formation of one A-center due to the decay of two divacancies. That is, $\Delta N_{V_2}/\Delta N_A = 2$, where ΔN_{V_2} is the concentration of decayed divacancies and ΔN_A is the concentration of A-centers formed at the DV decay. After the decay of divacancies with the concentration $N_{V_2} \approx 2 \times 10^{13}$ cm^{-3}, there appear A-centers with the concentration $N_A \approx 1 \times 10^{13}$ cm^{-3} (Fig. 3, curves *1* and *2*).

The decay of a divacancy results in the formation of two vacancies, whereas the generation of one A-center requires only one of them. Therefore A-centers are formed with the use of 25% of annealed divacancies. The rest of them are evidently annealed by means of their conversion to other defects, for example V_2O. The V_2O complex is formed in several stages. First, one of two vacancies in the complex located close to the Si–O–Si bond forms an A-center according to the reaction O+V → A-center. After that, the second vacancy is added: $A(V+) + V \to V_2$O. V_2O complexes correspond to the energy level E_C–(0.5±0.05) eV and are annealed at $T_{\rm ann}$=620 K similarly to A-centers. The effectiveness of introducing these centers depends on the oxygen concentration [2]. It is possible that the annealing of divacancies takes place by means of their conversion to "phosphorus + V_2" (PV_2) complexes. As is known, the latter are formed in n-Si crystals in the process of long-term irradiation or isochronous annealing of irradiated samples. PV_2 complexes bring the acceptor level E_V+0.34 eV to the lower half of the forbidden band and are annealed in the range $T_{\rm ann}$ = 400–500 °C [27, 28].

In the samples irradiated at room temperature, there is no negative annealing on the curve $N_A(T_{\rm ann})$ in the range $T_{\rm ann}$ = 250–300 °C in the region of DV decay, which is probably due to the large value of the ratio $N_A/N_{V_2} \approx 2$.

At such a relation between the concentrations of A-centers and DVs, the dissociation of one fourth of divacancies cannot considerably affect the concentration of A-centers.

As was already noted, in boron-doped p-Si crystals, DVs are completely annealed due to their conversion to BV_2 complexes.

The specific character of the DV annealing in irradiated n-Si crystals (annealing through two mechanisms) allows one to assume that the binding energy between the components of V_2^+ in p-Si crystals exceeds that in n-Si crystals with prevailing negative DVs. It is possible that the concentration of sinks and the effectiveness of capture of divacancies by the former without the decay of those diffusing in the crystal is higher in p-Si samples as compared to n-Si crystals.

As one can see from curve *2* of Fig. 4, the concentrations of A-centers in n-Si samples irradiated with 25-MeV protons ($\Phi = 2.7\times10^{12}$ cm^{-2}) and those irradiated with 2.2-MeV electrons change in different ways. Due to the decay of E-centers, the concentration of A-centers does not change. The peculiarities of the isochronous annealing of A-centers can be explained by the existence of disordered regions (DR) in silicon crystals irradiated with high-energy protons. DRs represent effective sinks for vacancies migrating in the crystal after the dissociation of E-centers and decrease their participation in the additional formation of A-centers [29].

At the high-energy irradiation of n-Si crystals, divacancies are formed due to both cascade and diffusion mechanisms [30]. That is why their total number in the case of high-energy irradiation is larger than under low-energy one. In spite of this fact, the concentration of isolated electrically active divacancies in crystals irradiated by high-energy particles is somewhat lower than in the samples irradiated by low-energy electrons (see Figs. 4 and 2, curves *3* and *2*, respectively). It is due to the fact that the majority of divacancies under the high-energy irradiation is spent for the formation of DR cores and other vacancy associates [31].

DVs manifest no electrical activity in the DR core. As one can see from Fig. 4, the concentrations of A-centers and isolated divacancies (curves *2* and *3*, respectively) are related as $N_A/N_{V_2} \approx 2.5$, that is why no negative annealing of A-centers is observed in the region of the DV decay. As concerns DRs, they are completely annealed at 570 °C under high irradiation dozes, at which DRs overlap, and fragments of their decay cannot participate in the additional formation of A-centers [32]. On the contrary, being effective sinks for mono- and divacancies, they decrease the participation of DVs and products of their decay – monovacancies – in the additional formation of V$_2$O and A-centers, respectively.

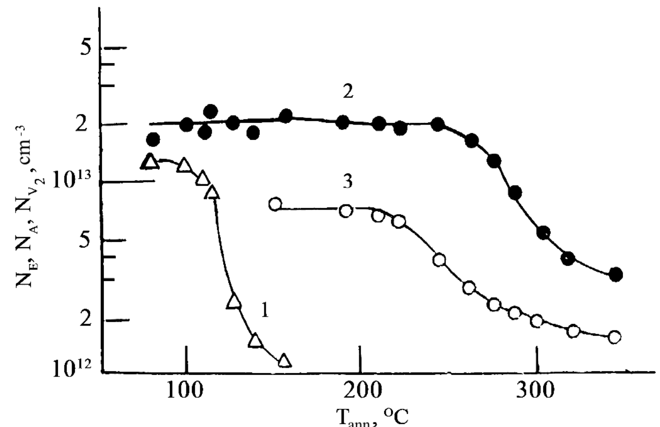

Fig. 4. Concentrations of E-centers (*1*), A-centers (*2*), and divacancies (*3*) as functions of the IA temperature in n-Si samples irradiated by 25-MeV protons at $T_{\rm irr}$ = 300 K. $\Phi_p = 2.7\times10^{12}$ cm^{-2}

4. Conclusions

The performed researches allow one to assume that the majority of divacancies in irradiated n-Si crystals are annealed by means of their conversion to other complexes. In n-Si, they can convert to DRs of the V_2O or PV_2 type.

A small part (25%) of divacancies is annealed via another mechanism – due to their dissociation into separate monovacancies, which results, in our case, in the negative annealing of A-centers.

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ДВА КАНАЛИ ВІДПАЛУ ДИВАКАНСІЙ В ОПРОМІНЕНИХ КРИСТАЛАХ КРЕМНІЮ n-ТИПУ

Т.А. Пагава, Н.Т. Бжалава, Н.И. Майсурадзе, Д.З. Хочолава, Л.С. Чхартішвілі

Р е з ю м е

Досліджено зразки кремнію n-типу провідності, що одержані методом зонної плавки, з концентрацією основних носіїв струму $6{\cdot}10^{13}$ см$^{-3}$, опромінених електронами з енергією 2 МеВ. Показано, що в опромінених зразках кремнію n-Si дивакансії відпалюються по двох каналах: шляхом їх конверсії в інші комплекси (V_2O чи PV_2) та дисоціацією на окремі моновакансії.