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Formation of radiation defects in silicon structures under low-intensity electron irradiation

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Abstract

Formation of A-centres and divacancies in silicon p^+–n–n^+ structures was investigated for 4 MeV electron irradiation in the low-intensity range of 10^{11}–5×10^{12} cm^{-2} s^{-1}. It is shown that the introduction rates of both A-centres and divacancies increase with intensity in this range and then saturate at intensities above 10^{12} cm^{-2} s^{-1}. Using the data from the literature the introduction rates of these defects are discussed in a wide range of intensities of electron irradiation of 10^{11}–10^{15} cm^{-2} s^{-1}, indicating a consistent role of carbon interstitial atoms and electron-enhanced migration of Si self-interstitials in the observed behaviour of introduction rates.

1. Introduction

Among various radiation defects (RDs) in silicon and silicon structures, the divacancy (W) and the A-centre (vacancy + oxygen pair) have been studied extensively versus intensity, J, and other conditions of electron irradiation [1–11] and a number of peculiarities of their formation have been revealed. In particular, for electrons with energy $\geqslant$3 MeV, which is able to create divacancies directly [1], the introduction rate $\eta(J)$ of divacancies in Czochralski-grown silicon was found to be practically independent of the intensity of electron irradiation in a broad range of intensities ($J > 10^{13}$ cm^{-2} s^{-1}) [5]. The simplest explanation is that the indirect formation of divacancies, which occurs by the merging of two vacancies created separately and, therefore, depends on the square of intensity of electron irradiation, is presumably overwhelmed by the formation of vacancy + oxygen pairs in the Czochralski-grown silicon, where the concentration of oxygen ($>10^{17}$ cm^{-3}) exceeds that of vacancies by several orders of magnitude. According to estimations made in [9], the contribution of the indirect channel to divacancy formation is only 6% and it increases about sixfold in float-zone silicon with oxygen concentration less than 10^{16} cm^{-3}. However, these estimations were performed neglecting the decay of divacancies and A-centres, where, at least, carbon, which is another dominant impurity with the same concentrations as oxygen in both types of silicon, may play an important role.

In [6] three ranges of intensities were distinguished for the formation rates of A-centres for high-intensity ($J > 10^{14}$ cm^{-2} s^{-1}) 4.4 MeV electron irradiation: two ranges with $\eta(J) =$ const separated by one in which the introduction rate of A-centres decreases with intensity of electron irradiation. Such dependence was explained [6] by supposing the possibility of radiation enhancement of carbon migration that accelerates decay of A-centres through the reaction with carbon interstitial atoms.

In this respect, the electron-enhanced Si self-interstitial migration and the creation of additional interstitial impurities, including carbon, by these self-interstitials are well documented experimentally [12, 13] and theoretically [14–16]; this can be used with more confidence to interpret intensity dependences of defect introduction rates. It is also of interest to analyse introduction rates of A-centres and divacancies in the low-intensity range and to compare them with those from [5,6] for the high-intensity one.

This paper presents results of the deep-level transient capacitance spectroscopy (DLTS) studies of the formation of A-centres and divacancies in silicon p^+–n–n^+ structures for 4 MeV electron irradiation at low intensities of 10^{11}–5×10^{12} cm^{-2} s^{-1} that are of particular interest in radiation technology of silicon devices. The behaviour of defect

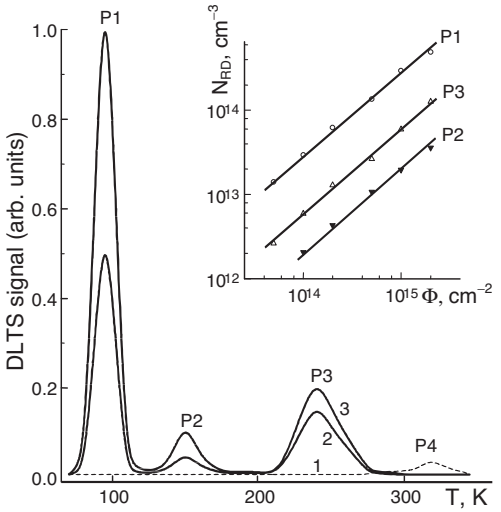

Figure 1. DLTS spectra of p^+–n–n^+ structures based on n-type silicon with resistivity of 2 Ω cm before (1) and after (2, 3) 4 MeV electron irradiation to a fluence of 10^{15} cm^{-2} at intensities of 5×10^{11} cm^{-2} s^{-1} (2) and 10^{12} cm^{-2} s^{-1} (3): P1, $E_c - 0.17$ eV; P2, $E_c - 0.23$ eV; P3, $E_c - 0.39$ eV; P4, $E_c - 0.48$ eV. In the inset the dependences of concentration of RD on irradiation fluence are given for the intensity of 10^{12} cm^{-2} s^{-1}.

introduction rates is then discussed in a wide range of intensities of electron irradiation, including those in [5, 6], emphasizing the role of Si and C interstitials in kinetics of the both A-centres and divacancies.

2. Experiment

Silicon diffusion p^+–n–n^+ structures were prepared from ∼350 μm thick wafers cut from n-type Czochralski-grown silicon ingots with diameters of 45 mm and resistivities of 2 and 10 Ω cm. The concentrations of oxygen and carbon were (2–5) × 10^{17} and (2–6) × 10^{17} cm^{-3}, respectively.

The p^+–n–n^+ structures were fabricated as follows. A mixture of a solution of aluminium salts in spirits and a water solution of boric acid was put on one of two opposite surfaces of wafers and the latter were then annealed at 1150 °C for 17 h. To avoid contamination of the wafer surfaces by uncontrollable impurities the annealings were performed in quartz tubes under flow of purified nitrogen (5–10 l h^{-1}). Due to a large difference in diffusion coefficients and solubility of B and Al in Si, the former forms a near-surface p^+-layer, but the latter a p–n junction. The resulting p-layer thickness was 80–90 μm according to estimations, suggesting a Gaussian-type distribution of Al impurities. Having performed standard procedures of polishing and cleaning of surfaces, a water solution of ortho-phosphorous acid was put on the other surfaces of the wafers and a short-time (0.5 h) diffusion annealing at 1000 °C was performed to obtain n^+-layers. Phosphorous–silicate glasses formed on the silicon surfaces immediately after such diffusion are known [17] to serve as efficient getters for such highly diffusive impurities as Cu and Au. These glass layers were then removed and samples with dimensions of 3.0 × 3.0 mm^2 were cut for studies.

The samples were irradiated with 4 MeV electrons to fluences of 10^{13}–10^{16} cm^{-2} at intensities of 10^{11}–5 × 10^{12} cm^{-2} s^{-1}. The irradiation was performed with a pulsed beam with frequency of 200 pulses s^{-1} each of 4 μs duration as in [5, 6]. The temperature of samples was kept not higher than 25 °C during irradiation.

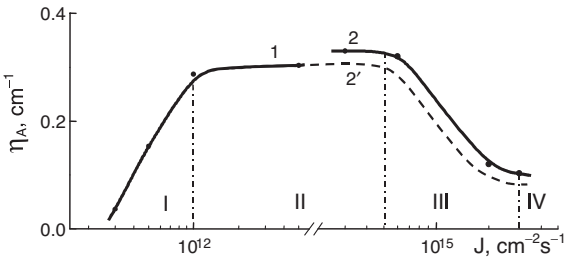

Figure 2. Introduction rates of A-centres versus intensity of 4 MeV electron irradiation: 1, our results; 2, the results of [6] for 4.4 MeV electron irradiation, 2′, the expected results of [6] for our experimental conditions and DLTS measurements.

Figure 1 presents typical DLTS spectra of the samples before (curve 1) and after (curves 2, 3) electron irradiation with the different intensities. The peak P4 is present only in the DLTS spectra of unirradiated samples and presumably corresponds to an unidentified thermal defect. This defect has concentration less than (2–3) × 10^{12} cm^{-3} and disappears after irradiation. Three peaks appear in the irradiated samples: P1 at 95 K, P2 at 150 K and P3 at 240 K. The peak P1 corresponds to the A-centre level $E_c - 0.17$ eV, but peaks P2 and P3 to levels $E_c - 0.23$ eV and $E_c - 0.39$ eV attributed to the two different charge states of the divacancy (the transitions W^{2-}/W^- and W^-/W^0, respectively [10]). As seen from figure 1, the increase of intensity of electron irradiation only results in the growth of peaks P1, P2 and P3 without any qualitative changes in the DLTS spectra. Note that a peak corresponding to the E-centre (vacancy + phosphorus) with level $E_c - 0.44$ eV was not revealed as compared with peak P3.

For the intensities considered in this paper the concentration of identified defects depends linearly on the fluence, $\Phi = Jt$ (t is the irradiation time), of electron irradiation. From these linear dependences (see the inset in figure 1) the introduction rates of A-centres and divacancies, $\eta_{RD} = J^{-1}\,dN_{RD}/dt = dN_{RD}/d\Phi$ in cm^{-1}, were obtained. The obtained data are given in figures 2 and 3 together with those of [5, 6] for the high-intensity electron irradiation. Note that each point in our curves is the mean value of results for five samples cut from the same wafers and irradiated under identical conditions.

3. Discussion

Despite the fact that n-type Czochralski-grown silicon species presumably from the same suppliers were used in both this work and [5, 6], there is no smooth transition from our curves to those of [5, 6] because of certain differences in irradiation conditions and measurement techniques. In [5, 6] defect concentrations were obtained from analysis of a temperature dependence of total concentration of electrons. This method is less accurate than DLTS measurements for discriminating contributions from particular defect levels. Consequently, a pronounced upper shift of the introduction rate of the

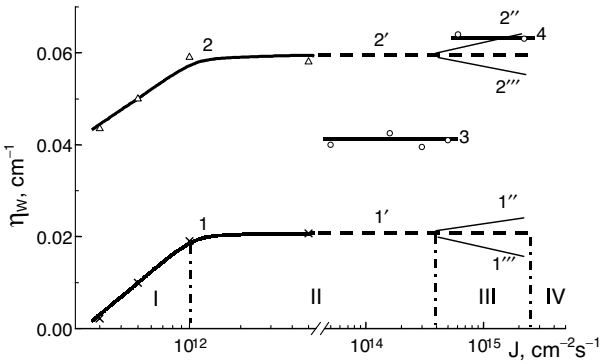

Figure 3. Introduction rates of divacancies versus intensity of 4 MeV electron irradiation: 1, 2, our results; 3, 4, results of [5] for 3 and 7 MeV electron irradiation, respectively; 1, 3, 4, $E_c - 0.23$ eV; 2, $E_c - 0.39$ eV; 1′, 2′, the expected results of [5] for our experimental conditions and DLTS measurements; 1″, 2″ or 1‴, 2‴, possible courses of experimental curves when the indirect channel of divacancy formation dominates decay of divacancies through interaction with carbon interstitials or vice versa.

divacancy level $E_c - 0.23$ eV in [5] as compared with that from our measurements (figure 3, cf curves 1 and 3, 4) is due to this demerit and substantial differences in electron beam energies. As for the A-centre (figure 2, cf curves 1 and 2), the mismatch of the curves is comparatively small and can be simply attributed to the fact that in [6] the irradiation was performed with slightly higher electron energies (4.4 MeV) than that (4 MeV) in our experiment.

Thus, we tend to think that if electron energies were the same in all three experiments and the DLTS measurements were used by the authors of [5, 6] as well, they would rather have curves very close to the dashed ones in figures 2 and 3. Therefore, the following discussion refers to the latter unless otherwise specified.

As seen from figures 2 and 3, we have found that the introduction rates of both A-centres and divacancies increase with the intensity of electron irradiation in the low intensity range, $J < 10^{12}$ cm^{-2} s^{-1}. For divacancies such an increase has been observed before for 0.9 MeV electron irradiation at high intensities $J > 10^{14}$ cm^{-2} s^{-1} [4]. The introduction rate of divacancies was about two orders of magnitude smaller than that ($\sim$0.1 cm^{-1}) of A-centres, but it manifested a square dependence on the intensity of electron irradiation. This was explained [4] by an influence of the intensity on charge states of vacancies and, consequently, on the introduction rate of divacancies through the indirect channel that dominates for the low-energy electron irradiation.

From this point of view, it is natural to expect a manifestation of the indirect channel in the high-intensity range of 10^{14}–10^{15} cm^{-2} s^{-1} also for high-energy electron irradiation that produces more vacancies than low-energy irradiation. However, the introduction rate of divacancies remains constant in this case [5] (figure 3), but that of A-centres, which is expected to be independent of the intensity, decreases and saturates above an intensity of 2×10^{15} cm^{-2} s^{-1} [6] (figure 2). How can these behaviours of introduction rates of divacancies and A-centres be explained consistently?

The decay of A-centres is commonly believed to occur primarily through interaction with the interstitial carbon atoms, and in [6] the decrease of introduction rate of A-centres with intensity was supposed to be due to an electron-enhanced migration of carbon interstitials at high intensities. However, the equilibrium concentration of carbon interstitial atoms appears to be exceedingly small, since they are very mobile and completely annealed at room temperature [2], occupying substitutional positions in the silicon lattice or entering into various defect complexes.

On the other hand, Si self-interstitial atoms created by electron irradiation, unlike carbon interstitials, indeed are known [12, 13] to exhibit electron-enhanced long-range migration; moreover, they end up with creation of additional interstitial impurities by a replacement reaction $Si_i + Imp_s = Si_s + Imp_i$, where i and s denote interstitial and substitutional atoms and Imp is an impurity. According to Bourgoin and Corbett [18], such migration can be assisted by charge state effects or charge state alternation effects. In the former case, under electron irradiation conditions, a non-equilibrium charge state with a lower barrier may be generated, supplying a faster migration path, and in the latter case the change in the charge state may drive the migration, for instance, when the defect stable configuration in one charge state is the saddle point configuration for migration between two stable positions for the other charge state, and vice versa. The possibility of both cases has been shown by *ab initio* [14, 15] and semi-empirical tight-binding [16] calculations.

Therefore, under high-intensity electron irradiation the reaction probability between Si and carbon interstitials should increase due to the charge state or the charge alternation effects that give rise to the enhanced migration of Si self-interstitials. This introduces an additional intensity dependence for the concentration of carbon interstitials and can by used to explain the observed peculiarities of introduction rates of A-centres and divacancies, provided that the divacancies also can decay through interaction with carbon interstitials. Here it is worth noting the existence of a complex of a divacancy with carbon atoms in the irradiated silicon according to the optically detected magnetic resonance studies [19].

Thus, due to the presence of powerful traps not only for vacancies, but also for carbon and silicon interstitials, neither of them is accumulated during irradiation and their concentrations are expected to be quasi-stationary:

$$dV/dt = 0; \qquad dI/dt = 0; \qquad dC_i/dt = 0. \quad (1)$$

For V and I (I represents Si_i) this means

$$V = N_{Si}\sigma_F\tau_v J; \qquad I = N_{Si}\sigma_F\tau_i J, \quad (2)$$

where N_{Si} is the concentration of silicon atoms; σ_F is the cross-section of formation of Frenkel pairs and τ_v and τ_i are lifetimes of vacancies and Si interstitials.

Kinetic equations for concentrations of carbon interstitials, A-centres and divacancies can then be written as follows (here for simplicity all non-equilibrium carbon interstitials, C_i', produced by Si self-interstitials are supposed to be trapped only by A-centres and divacancies; this does not cause any problems for the following rather qualitative discussions)

$$dC_i'/dt = \delta_{IC}\alpha\tau_i J C_s - \delta_{AC} A C_i' - \delta_{WC} W C_i',$$

$$dA/dt = \delta_{VO}\alpha\tau_v J O - \delta_{AC} A C_i - \delta_{AS} A S,$$

$$dW/dt = \beta J + \delta_{VV}(\alpha\tau_v J)^2 - \delta_{WC} W C_i - \delta_{WS} W S,$$

or, using the assumption (1) for carbon interstitials as well and dividing the latter two equations by J,

$$C_i = \delta_{IC}\alpha\tau_i J C_s/(\delta_{AC}A + \delta_{WC}W) + C_i^0, \quad (3)$$

$$dA/d\Phi = \delta_{VO}\alpha\tau_v O - \delta_{AC}\delta_{IC}\alpha\tau_i C_s \gamma A - \delta_{AC} A C_i^0 J^{-1} - \delta_{AS} A S J^{-1}, \quad (4)$$

$$dW/d\Phi = \beta + \delta_{VV}\alpha\tau_v(\alpha\tau_v J) - \delta_{WC}\delta_{IC}\alpha\tau_i C_s(1-\gamma)W - \delta_{WC} W C_i^0 J^{-1} - \delta_{WS} W S J^{-1}, \quad (5)$$

where $\alpha = N_{Si}\sigma_F$; β is the introduction rate of divacancies by the direct mechanism; δ_{VO}, δ_{VV} etc are constants of quasi-chemical reactions between V and oxygen, between two vacancies etc; $\gamma = \delta_{AC}A/(\delta_{AC}A + \delta_{WC}W)$ is the fraction of carbon interstitials that reacts with A-centres; S stands for all secondary traps (metal impurities and defects other than A-centres and divacancies) and C_i^0 is the equilibrium concentration of carbon interstitial atoms.

The whole region of intensities considered in the three experiments can be conveniently divided into the four ranges (figures 2 and 3). In the ranges I and II the reaction constants of defects are not yet influenced by the intensity, and the first two terms in (4) and the third one in (5) are independent of intensity. It is also obvious that the ratio of the second term in (5) to the first term in (4) $(\delta_{VV}\alpha\tau_v/\delta_{VO})(J/O)$, does not exceed 0.01 in these ranges, while the ratio of the experimental introduction rate of divacancies to that of A-centres (figures 2 and 3) is about 0.1. This enables one to conclude that the contribution of the indirect channel to the divacancy's introduction rate is negligible in the first two ranges of intensities. Then the increase and saturation of introduction rates in the ranges I and II, respectively, can be attributed to the two last terms in equations (4) and (5). The concentration of secondary traps and C_i^0 is most likely less than 10^{12} cm^{-3}, so the introduction rates for $J < 10^{12}$ cm^{-2} s^{-1} increase with decreasing $C_i^0\ J^{-1}$ and SJ^{-1} and saturate for $J > 10^{12}$ cm^{-2} s^{-1} when $C_i^0\ J^{-1}$ and $SJ^{-1} \ll 1$.

In the ranges III and IV one may expect not only the manifestation of the indirect channel of divacancy formation due to the factor J in the second term of equation (5), but an intensity dependence of reaction constants of defects because of the influence of the intensity of electron irradiation upon mobility and interaction of defects, shifting the balance of defect charge states. We use the most documented fact, the electron-enhanced migration of Si self-interstitial atoms [12–16], and suppose $\delta_{IC} = \delta_{IC}^0(1 + aJ)$, where $a \sim (10^{-15}$–$10^{-16})$ cm^2 s.

Then the decay of A-centres and divacancies through interaction with non-equilibrium carbon interstitials (the second term in (4) and the third term in (5)) will be dependent on the intensity of electron irradiation in the high-intensity range and results in a decrease of the introduction rates of both A-centres (figure 2) and divacancies (figure 3, curves 1‴ and 2‴) with intensity. However, in the case of divacancies, the contribution of the indirect channel (the second term in (5)) of divacancy formation also noticeably increases in the high-intensity range (figure 3, curves 1″ and 2″), which seems to compensate completely the above decrease of the divacancy's introduction rate.

Finally, in the high-intensity range IV the mobility of Si self-interstitials presumably reaches its maximum and saturates. This leads to saturation of the A-centre's introduction rate as well. However, in this case the introduction rate of divacancies may not increase because of competition between divacancy formation and formation of multivacancies or because of increasing of negatively charged vacancies; the latter, though they have lower migration barriers than neutral ones [12], will most likely avoid each other.

Of course, the above discussion is rather qualitative and needs additional experimental research and computer simulations. In particular, it is necessary to study samples with different concentrations of carbon impurities, as well as to obtain details of potential energy surfaces of reactions between Si self-interstitials and substitutional carbon and between carbon interstitials and A-centres and divacancies, for different charge states of these systems.

4. Conclusion

Formation of A-centres and divacancies in silicon p^+–n–n^+ structures was investigated for 4 MeV electron irradiation in the low-intensity range of 10^{11}–5×10^{12} cm^{-2} s^{-1}. The introduction rates of both A-centres and divacancies were found to increase with intensity in this range and then saturate at intensities above 10^{12} cm^{-2} s^{-1}. The behaviour of introduction rates has been discussed in a wide range of intensities of electron irradiation of 10^{11}–10^{15} cm^{-2} s^{-1} using also the results of other authors. Four ranges of intensities are distinguished and the roles of carbon interstitial atoms, electron-enhanced migration of Si self-interstitials and secondary traps were indicated in the observed behaviour of introduction rates of A-centres and divacancies.

References

[1] Corbett J W and Watkins G D 1965 *Phys. Rev.* A **138** 555
[2] Smirnov L S (ed) 1980 *Voprosi Radiatsionnoy Technologii Poluprovodnikov* (Novosibirsk: Nauka)
[3] Gerasimenko N N, Dvurechensky A B, Panov V I and Smirnov L S 1971 *Fiz. Tekh. Poluprovodn.* **5** 1644
[4] Kolesnikov N V, Lomasov V N and Malkhanov S E 1987 *Fiz. Tekh. Poluprovodn.* **21** 1136
Kolesnikov N V, Lomasov V N and Malkhanov S E 1989 *Fiz. Tekh. Poluprovodn.* **23** 1921
[5] Emtsev V V, Klinger P M, Mashovets T V and Mirazizyan K M 1990 *Fiz. Tekh. Poluprovodn.* **24** 1209
[6] Emtsev V V, Klinger P M and Mashovets T V 1991 *Fiz. Tekh. Poluprovodn.* **25** 45
[7] Emtsev V V, Klinger P M and Mirazizyan K M 1991 *Fiz. Tekh. Poluprovodn.* **25** 561
[8] Abdurakhmanov K P, Sherimbetov T, Dobrovinsky Yu M and Sagdullaev Kh U 1988 *Fiz. Tekh. Poluprovodn.* **22** 510
[9] Baranov A I, Vasil'ev A V, Komolova N I and Smagulova S A 1983 *Fiz. Tekh. Poluprovodn.* **17** 1663
[10] Svensson B G, Mohadjeri B, Hallen A, Svensson I H and Corbett J W 1991 *Phys. Rev.* B **43** 2292
[11] Avalos V and Dannefaer S 1998 *Phys. Rev.* B **58** 1331
[12] Watkins G D 1967 *Phys. Rev.* **155** 802
Watkins G D 1999 *Fiz. Tverd. Tela* **41** 826
[13] Bean A R, Newman R C and Smith R C 1970 *J. Phys. Chem. Solids* **31** 739
[14] Bar-Yam Y and Joannopoulos J D 1984 *Phys. Rev. Lett.* **52** 1129

[15] Car R, Kelly P J, Oshiyama A and Pantelides S T 1984 *Phys. Rev. Lett.* **52** 1814
[16] Khakimov Z M 1998 *Mater. Res. Soc. Symp. Proc. (Warrendale, PA)* vol 527 (Pittsburgh, PA: Materials Research Society) p 369
[17] Milnes A G 1973 *Deep Impurities in Semiconductors* (New York: Wiley)
[18] Bourgoin J C and Corbett J W 1978 *Radiat. Eff.* **36** 157
[19] Vlasenko L S 1999 *Fiz. Tverd. Tela* **41** 774