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Irradiation Enhancement of Electrical Properties of Passive Impurities in Silicon Crystals

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Authors' contributions

This work was carried out in collaboration between all authors. Author HNY managed works and experimental procedure. Author AAS performed measurements of charge carriers concentration. Authors VAS and NEG performed optical measurements. Author VAS took part in interpretation of experimental results and writing of article. All authors read and approved the manuscript.

Original Research Article

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ABSTRACT

Radiation defect formation processes in silicon crystals for the cases when concentrations of electrical non-active impurities (oxygen, carbon) prevail over main impurities determining silicon conductivity, are being covered in this paper. The role of interstitial atoms and vacancies, oxygen and impurity atoms in formation of radiation defects of A- and E-centers and divacancies, as well as their influence on electrical and optical properties of silicon crystals are shown. Energy levels of radiation defects in forbidden gap of silicon and their introduction rates were defined based on temperature dependencies of the concentrations of charge carriers at different irradiation doses. The capture probability of interstitial atoms and vacancies by main and passive impurities is taking into account. In addition to known A- and E-centers, along with disordered regions (clusters), a new radiation centers with energetic levels at E_c - 0,33eV; E_c -0,40eV and E_c -0,22eV were detected and studied. The first level is connected with silicon interstitial atoms, whereas the second corresponds to divacancies and the last one is identified as divacancy + oxygen.

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1. INTRODUCTION

As numerous theoretical and experimental investigations suggest (e.g. [1-7]), the main effect of radiation influence on the semiconductor crystals, with the exception for GaAs, is high mobility of primary radiation defects: vacancies and interstitial atoms, with the mobility of the latter being highest, sometimes non-activation. During movement the primary defects react with crystal imperfections: dislocations and other impurities and form new stable defects which determine the properties of samples at the given temperature. The temperature increase leads to the reactions with primary point defects and formation of secondary defects which are stable at high temperatures, however further temperature raise returns crystal to the initial state. It is, however, difficult to achieve complete temperature annealing [8]. For silicon the most known reactions are vacancy capture by different defects: interstitial oxygen atoms with formation of A- centers (acceptor level E_c – 0.17eV); donor impurity substituted atoms (acceptor level E_c – 0.4eV); acceptor impurity substituted and inclusion atoms transmitted into substitution state as a result of vacancy capture; other vacancies with formation of divacancies (amphoteric center at the level E_v + 0.27eV as a donor and two acceptor levels at E_v + 0.51eV and E_c – 0.4eV). It is typical for interstitial silicon atoms to displace substituted impurity atoms from their positions and with the latter atoms becoming mobile and taking part in further reactions (for instance, carbon at room temperatures) [9-10].

These data suggest that in spite of electrical passivity of oxygen and carbon impurities in silicon crystals at free states, they are able to interact with primary radiation defects after irradiation and forming electrical active centers which affect crystal properties. In the present paper these problems are being discussed in detail along with analysis of conditions favoring formation of secondary radiation defects.

2. EXPERIMENTAL RESULTS

Hall effect and optical absorption measurements were carried out in silicon single crystals (Si) before and after irradiation by high energy electrons with different doses. The measurements of specific conductivity and concentration of free carriers in samples were carried out by standard 4-probe technique. Samples were irradiated in the linear electron accelerator of Yerevan Physics Institute. Concentration (N) of main current carriers, electro-conductivity (σ), mobility (μ) in silicon samples with different specific resistances (ρ) irradiated by different doses of electrons have been studied. Carrier concentration and mobility were calculated by N=1/R; μ= Rσ; σ = μNe, where R- Hall coefficient, e-electron charge. Irradiation dose was calculated by $\Phi = 6.25 \times 10^{12} \times I \times t/S$ el/cm^2, where I is mean current of the beam in μA (beam intensity), t – exposure time in seconds, S – cross section of the beam in cm^2.

In general, the introduction of radiation defects (RD) leads to the reduction of concentration and mobility of main carriers in crystal. The degree of variation of these parameters depends on the initial properties of the Si-samples, irradiation energy, dose and intensity. Regarding the irradiation energy it should be noted that at high electron energy, when RD clusters are formed, the corresponding centers are more efficient, and changes of parameters occur at lower doses. Energetic levels of RD in the forbidden gap of n-Si have been determined according to thermal dependency of carrier concentrations at different irradiation doses, taking into account the capture probability of vacancies by matrix and non-matrix atoms.

The optical measurements of silicon crystals (Si) were done on spectrometers SF-8 (Russian production) and UR-20 (German production), allowing recording the relative spectra of irradiated and non-irradiated samples in a double-beam mode, to prevent the overlaying of interfering spectra, for example, atmospheric vapors. Many optical absorption peaks were observed in the frequency range between 850 cm^{-1} and 1600 cm^{-1} in n-type (phosphorus-doped) Si crystals. Such peaks were very weak in Czochralski-grown Si (Cz - Si) crystals. This suggests that the mentioned peaks should be attributed to complexes of oxygen and vacancies since most vacancies in Cz - Si form pairs (A center) with oxygen because of the very high concentration of oxygen in those crystals. They disappeared as a result of annealing at temperatures above 175°C. Temperature dependencies of intensities of other peaks were studied. The investigation was focused, in particular, on three satellite bands in the region, located at 839 cm^{-1}, 833 cm^{-1} and 824 cm^{-1}, respectively, the annealing behavior of which was carefully monitored. The irradiation doses and the concentrations of carbon and oxygen in the samples have been chosen to monitor the radiation defect formation process. Single vacancies (and self-interstitials) are introduced at the rate of ~1 cm^{-1}, and divacancies at 0.5 cm^{-1}. Stable di-interstitials are formed when two self-interstitials are displaced in one damage event, and they are mobile at room temperature. In the initial stages of annealing the evolution of the point defects is caused by impurity trapping. The well-known W center is generated by restructuring within clusters, with a range of activation energies of about 1.3 eV to 1.6 eV, reflecting the complex nature of the clusters. Comparison of the defect center formation in oxygen-rich and low-oxygen silicon samples suggests that certain defects may be interstitial-related rather than vacancy-related. To a large extent, the radiation damage and annealing behavior may be factorized into point defects and cluster defects.

3. DISCUSSION

Infrared absorption spectra (IR) of irradiated samples suggest that along with appearance of new IR bands, responsible for electrical active centers, a decrease of 9μ and 16μ absorption bands is observed with the irradiation dose increase, which are known as interstitial oxygen atom and substituted carbon atom, respectively. This decrease indicates a direct involvement of oxygen and carbon atoms in the formation of secondary radiation defects.

The dependence of substituted carbon ($\triangle N_c$) and interstitial oxygen ($\triangle N_o$) atoms concentration change upon electron irradiation dose is presented in Fig. 1. The calculations of these concentrations were carried out by graduation formulas $N_O = 4.8 \times 10^{17}(\alpha_O - 0.5)$ cm^{-3} for oxygen [6] and $N_C = 1.05 \times 10^{17}(\alpha_C)$ for carbon [7] performing IR absorption measurements. Detailed absorption spectra of oxygen atoms at 9 μ before and after irradiation by different doses are presented in Fig. 2.

The behavior of the oxygen absorption band shows that its shape largely depends on way the post-radiation annealing is performed. The optimum annealing is when the sample is immediately cooled after being kept at 1300º for a sufficient time. This will prevent coagulation of O_i oxygen atoms [8]. In this case the oxygen absorption band is stipulated mainly by isolated O_i (the maximum of the band is located at 1106 cm^{-1} at room temperatures). If the crystal was immediately cooled without being kept at 1300ºC for sufficient time, then apart from O_i, other centers like S_iO_n (n=1,2,3,...) quasi-molecule or with carbon atom may be formed. They may also contribute to the absorption near 9 μ band. At the liquid helium temperature this band has a more distinct structure at the maxima at: 1082 cm^{-1}, 1104 cm^{-1}, 1128 cm^{-1}, 1135 cm^{-1}, 1180 cm^{-1}, 1206 cm^{-1}. This structure is not manifested at room temperature, although, obviously, it is not uniform.

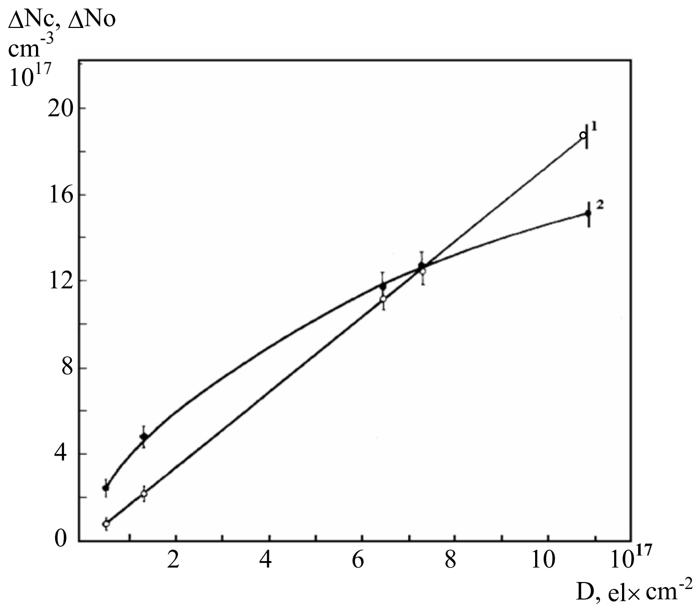

Fig. 1. Changes of substituted carbon (1) and interstitial oxygen (2) atoms concentrations in p-silicon (ρ= 250 Ohm · cm) depending on irradiation dose of electron with energy of 50 MeV"

Since it is difficult to control the oxygen atoms making up other quasi-molecules, the technique of measured absorption approximation was applied as a superposition of Gaussian bands. Its parameters, including location of maxima and number of bands, were estimated by the minimum value of mean squire error (RMSFE). The computer decomposition of main band at 9 μ (Fig. 2) revealed three components at frequencies 1098 cm^{-1}, 1106 cm^{-1}, and 1150 cm^{-1}, the first two being strongly sensitive to irradiation. They decrease at different rates depending on irradiation dose; this is the reason for change in the shape of 9μ band. These changes suggest that the whole oxygen in all quasi-molecules participates in defect formation.

It is known that the presence of electrically active radiation defects decreases the concentration and mobility of charge carriers in crystals. The change degree of these parameters depends on both main and non-active impurities in initial samples. This is demonstrated in Figs. 3 and 4, where the dose dependencies of charge carriers concentration and their mobility are presented in n-Si crystals with different initial specific resistances.

Figs. 3 and 4 show the existence of certain critical irradiation dose, after which sharp decrease of parameters occur which depends on both main doped and electrical passive impurities (oxygen, carbon). Energy levels of radiation defects in forbidden gap of silicon and their introduction rates were determined based on temperature dependencies of charge carriers concentrations at deferent irradiation doses. Capture probability of interstitial atoms and vacancies by main and passive impurities was taken into account. In addition to known A- and E-centers, along with disordered regions, a new radiation centers with energetic levels at E_c – 0.33eV; E_c -0.40eV and E_c -0.22eV were detected and studied. The first level is attributed to silicon interstitial atoms, the second corresponds to divacancies, and the last one is identified as divacancy + oxygen. The appearance of such center is explained by the fact that during irradiation process in silicon with high resistance (ρ>100 Ohm × см) more vacancies are created. Part of those vacancies are either able to connect together and be captured by oxygen atoms or form A-centers, then connect with other vacancy. At the end, in both cases a divacancy + oxygen complex is formed. The high concentration of vacancies, most probably, should be attributed to the high concentration of substituted carbon atoms. As optical measurements suggest the latter participates in reactions at irradiation process [9].

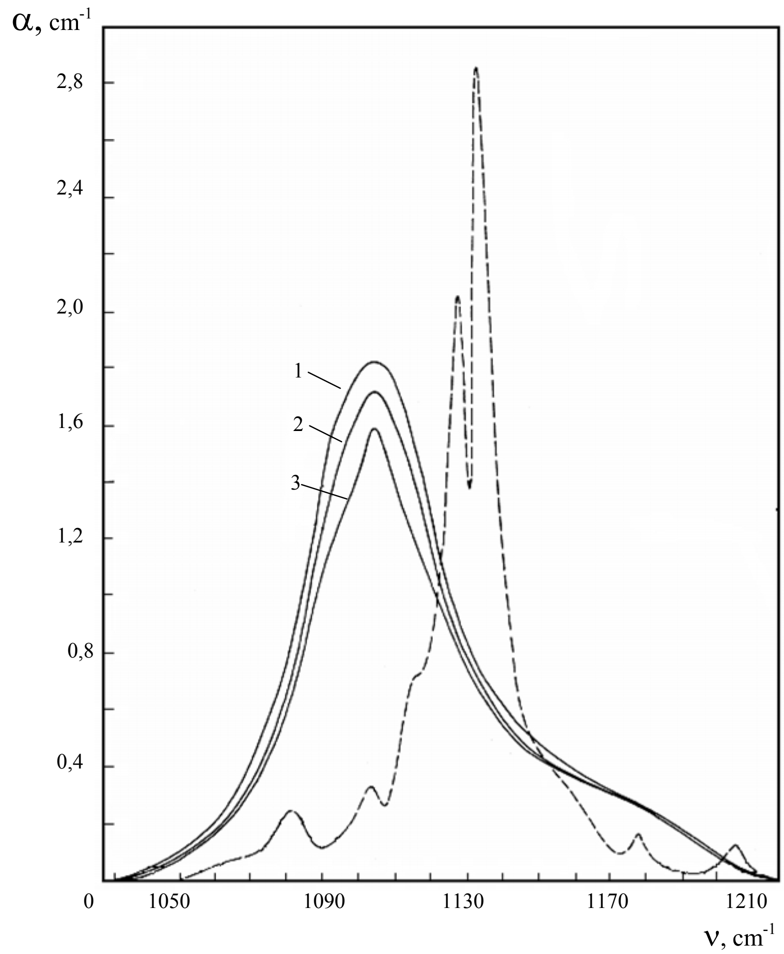

Fig. 2. Change of 9μ absorption band in p- Si (ρ= 250 Ohm×cm) at different doses of irradiation by electrons with 50 MeV energy: 1-initial, 2- 1.3 × 10^{17}el/cm^2, 3- 1.1 × 10^{18}el/cm^2 (dotted line is the fine structure of the band at liquid helium temperature)

The concentration of main impurity atoms in the silicon crystals under consideration was lower than that of electrically inactive oxygen and carbon. In addition, they are known as a trap for primary simple defects in silicon crystal. Therefore, it is interesting to study the behavior of vacancy to vacancy interaction depending on the concentrations of oxygen and carbon atoms. It has to be noted that the substitution carbon atoms C_S are effective traps for I_{Si} and at sufficiently low irradiation doses all generated I_{Si} strive to traps. Whereas the accumulation of vacancies (single or bonded in complexes) takes place linearly with dose they can compete with C_S at further accumulation when increase of vacancies concentration becomes sub-linear. At the same time, although at the beginning of the linear region of accumulation the vacancy generation rate does not depend on C_S, however the starting time of sub-linearity and its nature depend on C_S. Nevertheless, some evidence suggests that the vacancy introduction rate depends on traps even at the linear region of their accumulation [10]. This is especially obvious when dominating for V - V interaction is divacancy (V_2).

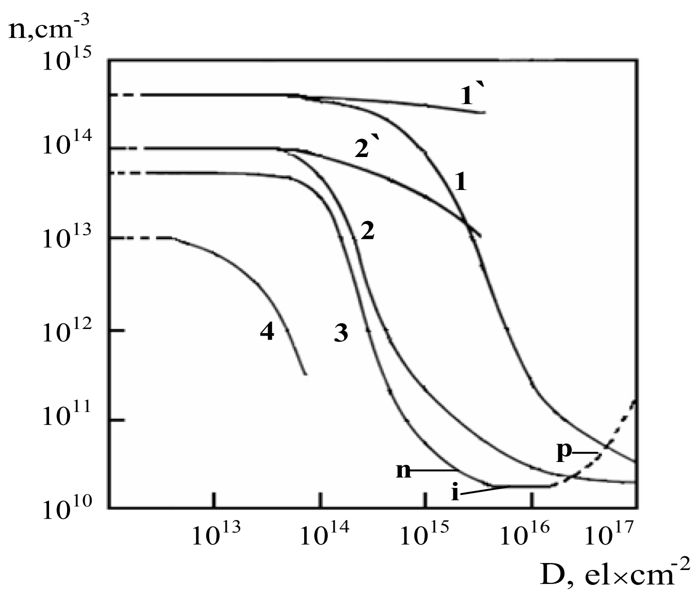

Fig. 3. Dose dependence of main carrier concentrations in n-Si irradiated by electrons with energies:

7, 5 MeV (1´ u 2´) and 50 MeV (1,2,3,4. T =300K):

1, 1´- ρ= 10 Ohm × cm ($N_O \approx 1.2 \times 10^{18}$ cm^{-3}, $N_C \approx 10^{17}$ cm^{-3});

2, 2´- ρ= 40 Ohm × cm ($N_O \approx 7 \times 10^{17}$ cm^{-3}, $N_C \approx 10^{17}$ cm^{-3});

3 - ρ= 100 Ohm × cm ($N_O \approx 7 \times 10^{17}$ cm^{-3}, $N_C \approx 3.2 \times 10^{17}$ cm^{-3});

4 - ρ= 450 Ohm × cm ($N_O < 10^{16}$ cm^{-3}, $N_C < 10^{17}$ cm^{-3})

The results of optical absorption measurements of divacancy concentration are presented in Fig. 5. As shown, there is a significant difference in introduction rates of divacancy for samples with different content of C_S and O in linear region of accumulation at the identical conditions of their irradiation. The linear introduction rate of divacancies is 0.362cm^{-1} (curve 1, Fig. 5) and decreases gradually to 0.110 cm^{-1} in the sequence of 2-5 curves (Fig. 5). Here linear regions of N_{V2}(D) dependencies directed to the beginning of coordinates are taken into account. The curve corresponding to minimal introduction rate of V_2, has quasi-linear region which doesn't cross the origin of coordinates, hence it isn't taken into account in the future analysis.

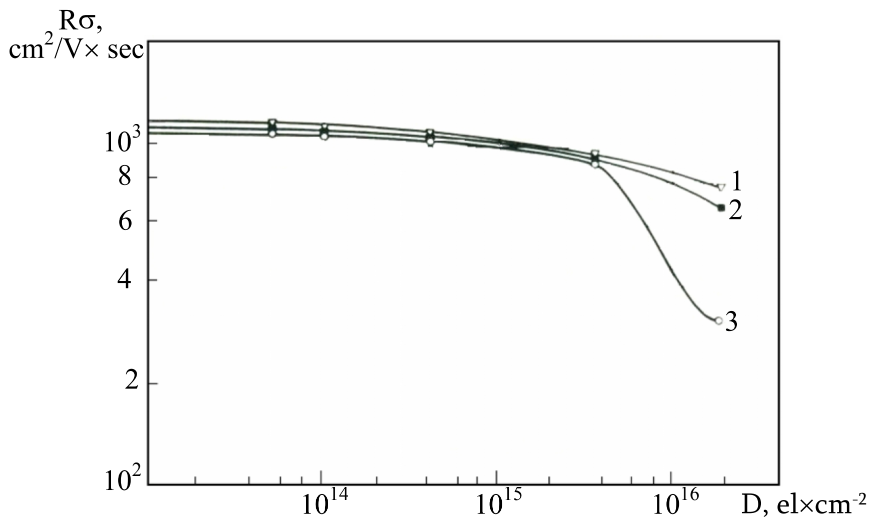

Fig. 4. Dose dependence of carrier mobility in n-Si with specific resistances: ρ= 100 Ohm × cm (1), ρ= 400 Ohm × cm (2) и ρ= 1000 Ohm × cm (3) irradiated by electrons with energy 50 MeV (T =300K)

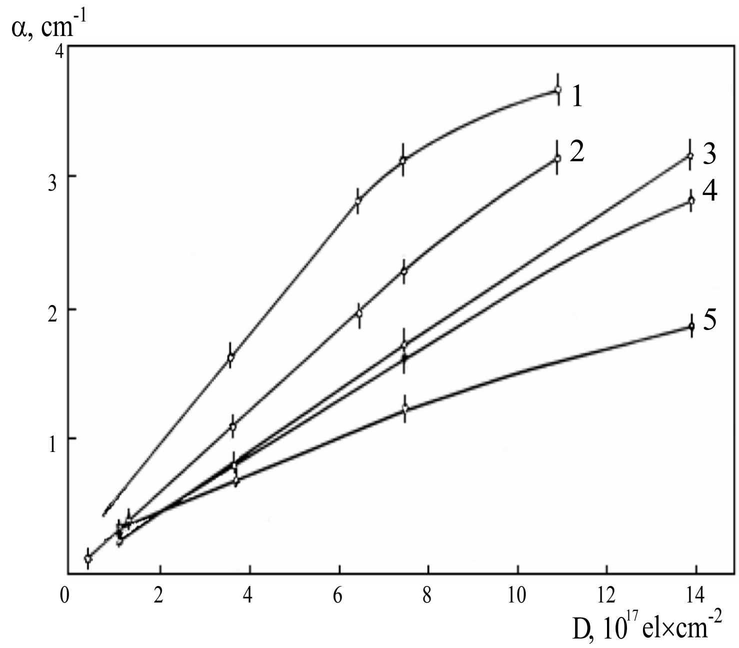

Fig. 5. Electron irradiation (energy 50 MeV) dose dependence of divacancy concentrations in Silicon:

1-S_i- p ($\rho \sim$ 5 Ohm $\times$ cm, $N_O \sim 1.5 \times 10^{18}$cm^{-3}, $N_C \sim 7 \times 10^{17}$ cm^{-3});
2- S_i- p ($\rho \sim$ 250 Ohm $\times$ cm, $N_O \sim 6 \times 10^{17}$ cm^{-3}, $N_C \sim 7 \times 10^{17}$ cm^{-3});
3- S_i- p ($\rho \sim$ 20 Ohm x cm, $N_O \sim 1.3 \times 10^{18}$ cm^{-3}, $N_C \sim 1.1 \times 10^{17}$ cm^{-3});
4- S_i- n ($\rho \sim$ 100 Ohm x cm, $N_O \sim 7 \times 10^{17}$ cm^{-3}, $N_C \sim 3.2 \times 10^{17}$ cm^{-3});
5- S_i- n ($\rho \sim$ 450 Ohm x cm, $N_O < 10^{16}$ cm^{-3}, $N_C < 10^{17}$ cm^{-3})

It is obvious from given characteristics of investigated samples that divacancy introduction rate tends to increase with increase of both oxygen and carbon concentrations.

The dependence of divacancy concentration on concentration of removed or substituted carbon atoms in silicon irradiated by electrons with energy 50MeV and dose 1.1×10^{18}el/cm^2 is illustrated in Fig. 6. It shows that the introduction of divacancies linearly increases with removed carbon concentration even at large irradiation doses in cluster region of energies.

From the data on Fig. 6 one can assume that the influence of concentration of traps for interstitial atoms on the divacancy introduction rate at the linear region of their accumulation is possible for cases when genetic Frenkel pairs recombination is more effective. Indeed, due to small spatial distance of pairs at the time of their origin, they have higher probability of inter - annihilation than cross-row recombination. The presence of traps capturing interstitial atoms prevents vacancies from annihilation. Nevertheless, theoretical evidence suggests lower influence of traps on the vacancy and divacancy introduction rate than obtained in experiment [10]. From physical point of view this is explained by the low probability for the return of a randomly moving particle in the infinite three - dimensional space, to the initial point. It tends to zero even at $t\rightarrow\infty$. The particle “will get lost” in the infinite volume and will not return to the point of origin even in the absence of any traps. Hence the role of traps in recombination of genetic pairs is negligible even when traps essentially decrease “cross-row” recombination.

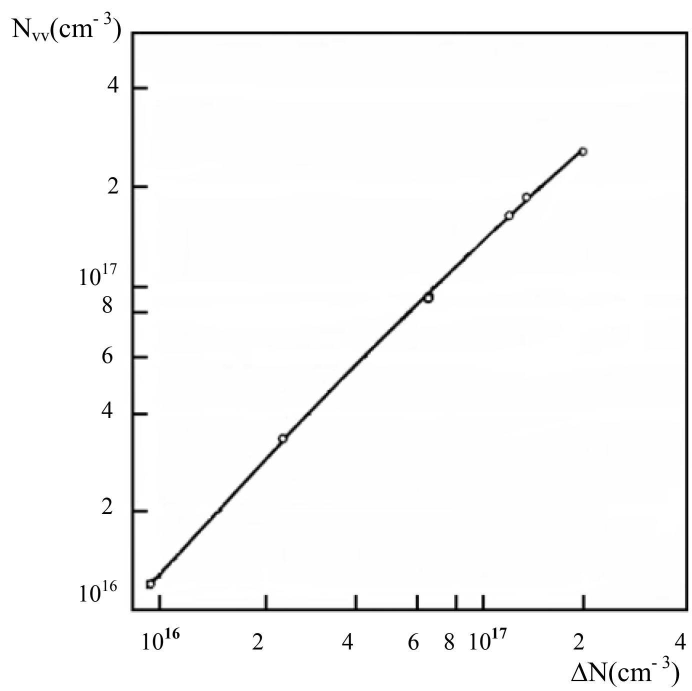

Fig. 6. Dependence of di-vacancy concentration on concentration of removed substitution carbon atoms in silicon irradiated by electrons with energy 50MeV and dose 1.1 × 10^{18}el/cm^2

For a one - dimensional diffusion of interstitial atom the situation is different. In accordance with the limit theorem of random walk in a one - dimensional space the probability of a particle to return to its point of origin is 1, and in the absence of traps the recombination of genetic pairs certainly takes place. Such probability realizes in cubic lattice as a craudion configuration (two atoms at both sides in normal state at small distance). This “incorporation” of a spare atom in an atomic chain destroys the symmetry of the system and leads to non-equivalency of atomic chains in three-dimensional space. To sum up, it can be stated that in real life there is a one - dimensional thermal diffusion of silicon atoms displaced by irradiation [3].

4. CONCLUSION

The character of radiation defect formation in Si crystals almost looks like for all samples irrespective of specific resistance and irradiation energies from point defect to cluster (disordered region) formation.

The introduction rates of I, V, V_2 (divacancy) were determined in irradiated silicon crystals containing dominating electrically passive impurities: substitution carbon atoms Cs and inclusion oxygen atoms O_I. Concentrations of Cs, O_I and V_2 were measured by IR-absorption bands.

Main experimental finding: irradiation of samples under identical conditions leads to significant difference in V_2 introduction rate at the linear region of V_2 dependence on dose (Fig. 5). The analysis of impurity influence on divacancy introduction rate gives a one - dimensional diffusion of additional interstitial atoms which are ordered in atomic chains in configurations of double and triple grouping bonded atoms.

Thus, aforementioned results can be attributed to efficient capture of removed silicon atoms Si_I by impurity atoms (in particular, electrically non active). According to [6,7] $Si_I + C_s \rightarrow Si_S + C_I$ reaction is possible as well as capture of Si_I by oxygen atoms O_I [10]. It can be concluded from the data on Figs. 2 and 3 that both channels for capture of Si_I are effective. At the same time, decrease of Si_I absorption bands due to O_I and Cs is observed with increase of electron irradiation dose. In addition, the capture of Si_I atoms by impurity prevents their recombination with vacancy and contributes to the V_2 accumulation.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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