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Kinetics of self-interstitials reactions in p-type silicon irradiated with alpha particles

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ABSTRACT

New findings on the self-interstitial migration in p-type silicon are presented. They are based on experimental studies of the formation kinetics of defects related to interstitial carbon after irradiation with alpha particles. The main parameters characterizing the interaction rate of silicon self-interstitials with substitutional carbon atoms have been determined. A preliminary interpretation of the experimental data is given. The interpretation takes into account different diffusivities of self-interstitials in their singly and doubly ionized states.

1. Introduction

Knowledge of migration characteristics for native defects in silicon is important when describing diffusion and doping processes at high temperatures [1]. Migration characteristics of the silicon vacancy are well known from radiation experiments [2] and help to evaluate any vacancy contribution to self-diffusion at high temperatures [3]. The information on the migration of the silicon self-interstitial (Si_i) is less definite. It has been found that it can migrate even at liquid helium temperatures under very weak electronic excitation [2]. Earlier theoretical calculations had predicted relatively high migration energy for doubly positively charged self-interstitials [4]. That prediction has been confirmed with calculations performed in recent work (see Refs. [5,6] and references therein). In experimental studies, Mukashev et al. [7,8] found that the Si self-interstitials actually have a rather low mobility in p-type silicon irradiated with protons or alpha-particles. However, the group did not study the kinetics of the Si_i disappearance in detail and some of their results cannot be interpreted unambiguously and need further investigation. The aim of this work is to obtain new information on the kinetics of reactions related to the Si_i migration at near room-temperature.

2. Experimental details

Planar n^+–p–p^+ diode structures made of epitaxial silicon have been used in our experiments. The hole concentration in the p-region was about $1.0\times10^{15}\,cm^{-3}$. Using the method described in Ref. [9] the oxygen content was evaluated as about $2.3\times10^{17}\,cm^{-3}$. The carbon concentration was below the detection limit of $5\times10^{16}\,cm^{-3}$.

Irradiations with alpha-particles of a Pu-239 surface source were performed at about 290 K or slightly less. The alpha-particle energies were 5.144 and 5.157 MeV. Damage distribution for this kind of irradiation source was described in Refs. [9,10]. To determine the trap parameters we used a least-square procedure which allows evaluation of the parameters of several DLTS peaks simultaneously.

Isochronal annealing studies were performed in the temperature range of 280–380 K. The duration of each annealing step was 15 min.

3. Experimental results

Fig. 1 shows DLTS peaks of the dominant majority carrier traps, which were observed in irradiated structures after different treatments. Their energy levels are $E_v+0.19$ eV (H019), $E_v+0.28$ eV (H028) and $E_v+0.35$ eV (H035) and in accordance with the literature [11] they can be attributed to the divacancy $V_2(+/0)$, interstitial carbon $C_i(+/0)$ and a interstitial carbon–interstitial oxygen complex $C_iO_i(+/0)$, respectively.

As seen from Fig. 1 practically no peak related to a interstitial carbon atom H028 was observed immediately after alpha-irradiation: only H019 and H035x peaks are seen. The H035x peak position is close to that one of the H035 peak but does not exactly coincide with it [13]. The absence of the H028 peak and the low intensity of the H035 peak evidenced that practically only very little C_i has been formed during irradiation. However the H028

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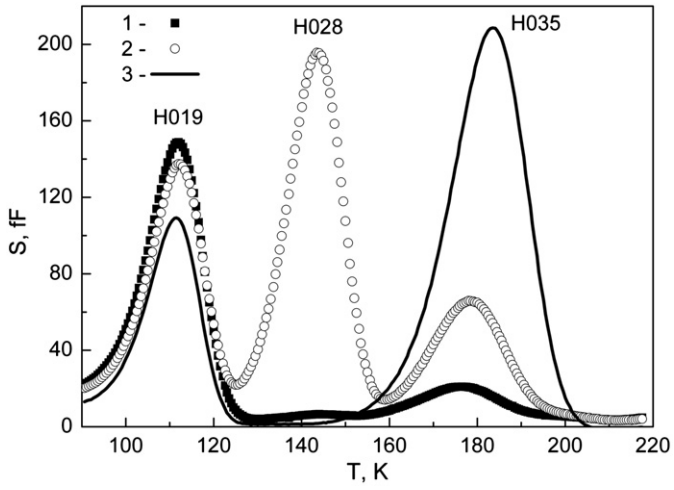

Fig. 1. DLTS spectra for a p-type Si sample irradiated with alpha-particles of Pu-239 source during 400 min at 15–20 °C measured immediately after irradiation (1), after forward injection at 80 K (2) and after subsequent annealing at 373 K for 30 min (3). Measurement settings were: emission rate window $e_w=19\ s^{-1}$, bias change $-5\rightarrow 0$ V, and filling pulse duration $t_p=10$ ms.

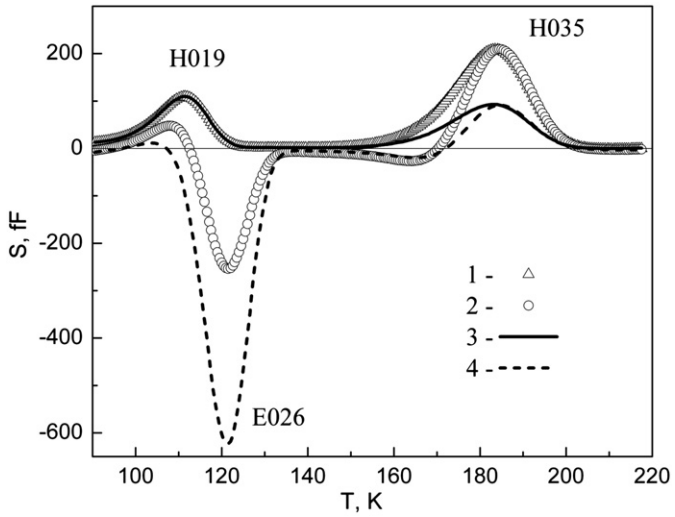

Fig. 2. DLTS spectra for the p-type Si samples irradiated with alpha-particles of Pu-239 source during 400 min at 15–20 °C measured after thermal annealing at 373 K with (curves 1 and 2) and without (curves 3 and 4) post-irradiation current injection at 80 K. Measurement settings were: emission rate window $e_w=19\ s^{-1}$, bias change $-5\rightarrow 0$ V (curves 1 and 3) and $-5\rightarrow +2$ V (curves 2 and 4), filling pulse duration $t_p=10$ ms.

peak appears after post-irradiation forward current pulse at 80 K. After subsequent thermal annealing at 373 K the H028 peak disappears and the H035 peak appears with the ratio close to 1:1 (Fig. 1) which is a consequence of the following reaction: $C_i+O_i\rightarrow C_iO_i$. A small difference between the heights of H028 and H035 peaks could arise due to another small DLTS peak superimposed with H035. The C_i and C_iO_i concentrations in the diode regions monitored by DLTS were of $2.0–2.5\times 10^{13}\ cm^{-3}$.

Therefore these data are in agreement with the results of Refs. [7,8] on a low Si_i mobility at $T<300$ K and with the well known recombination enhanced migration of Si_i [2].

Under the forward current injection, the ratio of Si_i capture radii by sustitutional boron (R_{IB}) and carbon (R_{IC}) is different when compared to this ratio at thermal equilibrium conditions. This difference is apparent in the DLTS spectra shown in Fig. 2. From Fig. 2 one can see that when the Si self-interstitials migrate at thermal equilibrium they have a higher ratio R_{IB}/R_{IC} than under forward current injection. If we suggest that R_{IC} does not depend on the Si_i charge state then we can draw a conclusion on higher R_{IB} in thermal equilibrium. This fact is in agreement with theoretical studies [4–6] which predict a low Si_i diffusivity in the doubly ionized charge state and the higher one in less positive charge state.

To determine the kinetic parameters of Si_i reactions at $T>300$ K we have carried out studies of isochronal and isothermal annealing. Because of the extreme sensitivity of Si_i to electron injection we were able to monitor only majority carrier traps under annealing. That is why the appearance of mobile Si_i was monitored by the appearance of C_i and its complexes C_iO_i and $C_iO_i^*$. The latter one is a metastable configuration of C_iO_i [12,13].

We suggest that during annealing the total concentration of all the C_i related complexes is changed as

$$[C_i]+[C_iO_i^*]+[C_iO_i]=C_{i0}+\eta_0[Si_i]_0\{1-\exp(-\tau/\tau_I)\} \quad (1)$$

where C_{i0} is the total concentration of all the carbon related defects observed immediately after irradiation and

$$\eta_0=\frac{K_{IC}[C_s]}{K_{IC}[C_s]+K_{IB}[B_s]+K_{IT}[T]}$$

is a fraction of the Si self-interstitials, which reacts with substitutional carbon. Here we suppose that during annealing the Si self-interstitials can react with sustitutional boron (B_s), carbon (C_s) and another undetermined trap (T). The time constant of annealing is denoted as τ_I.

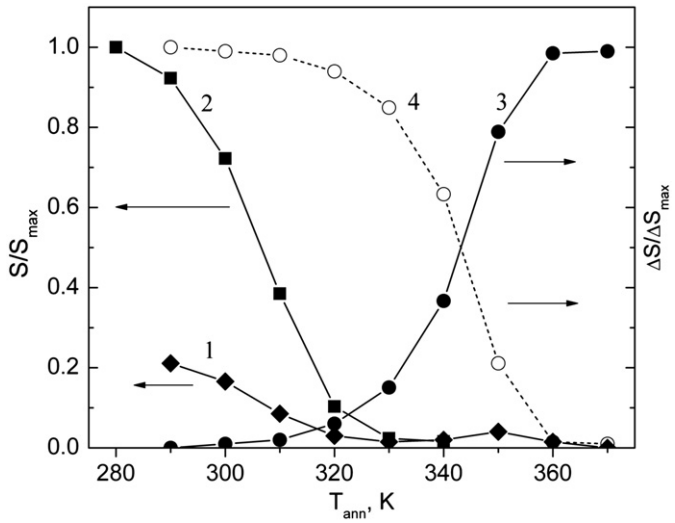

Fig. 3. Evolution of concentrations of carbon related centers during isochronal annealing of n^+–p diodes. Curve 1 represents evolution of H029 peak under thermal annealing. Curve 2 represents evolution of H029 peak under thermal annealing after preliminary current injection performed immediately after irradiation obtained on an identical sample. Curve 3 represents the increase in the total concentration of carbon related centers under thermal annealing. Curve 4 is calculated from curve 3 according to Eq. (2).

Curve 3 in Fig. 3 shows an increase in the total concentration of all carbon related complexes (C_i, $C_iO_i^*$ and C_iO_i) with annealing temperature formed due to an interaction with the self-interstitials remained immobile immediately after the irradiation. Assuming that all C_i are generated by reaction with self-interstitials taken into account by Eq. (1), we can calculate the concentration of self-interstitials that have reacted with substitutional carbon during the annealing as

$$\Delta S_I(T_{ann})=\Delta S_{C_iO_i}(100\,^\circ C)-\Delta S_{C_i}(T_{ann})-\Delta S_{C_iO_i^*}(T_{ann})-\Delta S_{C_iO_i}(T_{ann}) \quad (2)$$

where $\Delta S_X(T_{ann})=S_X(T_{ann})-S_X(\textit{as-irradiated})$ is the increment of the amplitude of X-peak, $X=C_i$, $C_iO_i^*$ or C_iO_i after annealing at T_{ann}.

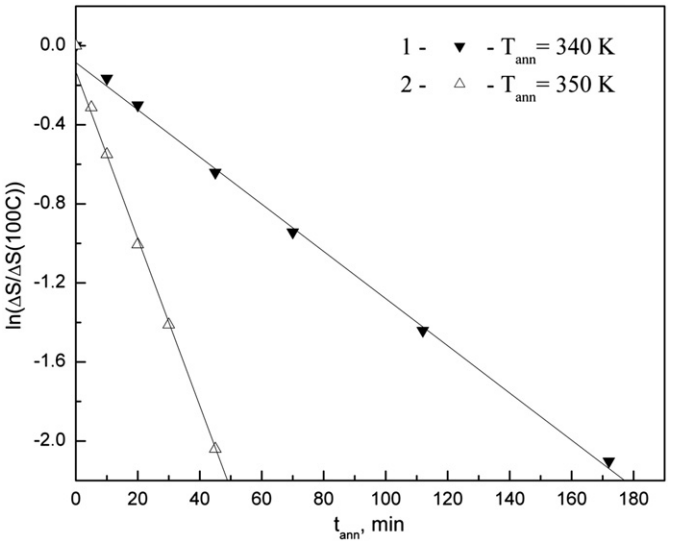

Fig. 4. Decrease in a normalized concentration of the Si self-interstitials reacted with substitutional carbon during the isothermal annealing at 340 K (1) and 350 K (2). Solid lines represent a linear fit of the experimental data.

Note, that the values of $\Delta S_X(T_{ann})$ for C_i and $C_iO_i^*$ can be positive or negative. So we used not the total concentration of C_i related peaks but the difference between the peak heights.

As seen in Fig. 3 although at annealing temperatures lower than 310 K the concentration of C_i decreases, the total concentration of carbon related defects does not change, essentially due to an increase in the concentration of other carbon complexes. The calculated dependence of ΔS_I on annealing temperature is shown by curve 4 in Fig. 3. As seen from this figure the rate of self-interstitials disappearance in thermal equilibrium is much lower than that one for interstitial carbon. About 90 % of the Si_i disappearance obeys an exponential law (Fig. 4).

Suggesting that $\tau_{ann}(T)$ obeys Arrhenius law

$$\frac{1}{\tau_{ann}} = A_{ann}\exp\left(-\frac{E_{ann}}{kT}\right) \tag{3}$$

we can fit our experimental isochronal annealing data. Fitting curves are also plotted with lines in Fig. 3. The obtained activation energy was equal to the value of 1.2 eV. The corresponding value of the pre-exponential factor A_{ann} in Eq. (3) is $A_{ann} \approx 1.2 \times 10^{14}\,s^{-1}$. From isothermal annealing data we have obtained $E_{ann}=1.3$ eV and $A_{ann} \approx 3.5 \times 10^{15}\,s^{-1}$. The difference can be related to a small initial fast drop of self-interstitial concentration seen in Fig. 4, which is an error of 0.1 eV for E_{ann} value determined from isochronal annealing measurements.

4. Discussion

These values of pre-exponential factor are typical or even higher if the annealing process is limited by the dissociation or reconfiguration of a defect complex. If the annealing process is limited by a long range migration of a defect the pre-exponential factor is expected to have a much lower value. For example while fitting the annealing curve for C_i annealing (curve 2 in Fig. 3) we obtained a pre-exponential factor of about $10^{10}\,s^{-1}$. However we cannot interpret the obtained activation energy unambiguously as an energy barrier for a self-interstitial complex dissociation. As follows from other experimental results [8,14] there is a material dependence of annealing temperature for Si_i. This fact suggests that the obtained value of A_{ann} can correspond to a diffusion limited process of Si_i reactions in alpha-irradiated crystals.

The problem of a proper interpretation of the relatively high pre-exponential factor for interstitial defects reactions appeared earlier in studies of interstitial boron annealing in electron irradiated silicon [15]. As a possible origin of the about $\sim 10^3$ increase in the pre-exponential factor the authors of Ref. [15] suggested the contribution of the Bourgoin mechanism to interstitial boron diffusion. However they also noted that experimental results obtained for B_i annealing require an alternate explanation.

Our explanation of the Si_i annealing features is based on the fact that there is a very strong difference between the diffusivities of self-interstitials in different charge states. Theoretical calculations [4–6] show that self-interstitials have a relatively high migration barrier in the doubly ionized state (Si_i^{++}) and much lower barriers for the other charge states. It suggests (see Ref. [1]) that the resulting diffusivity D_I during Si_i annealing should be written as the sum

$$D_I = f^{++}D_{I^{++}} + f^{+}D_{I^{+}} + f^{0}D_{I^{0}} \tag{4}$$

where f^{++}, f^{+} and f^0 are occupancy numbers and $D_{I^{++}}$, $D_{I^{+}}$ and D_{I^0} are diffusivities of self-interstitials in their doubly positive, singly positive and neutral charge states, respectively.

As follows from theoretical calculations [5] both donor levels ($E_I(+/++)$ and $E_I(0/+)$) of self-interstitials are located in the range of $E_c-(0.3–0.40)$ eV, where E_c is the conduction band edge. It should be also noted that these values are consistent with the experimental data for radiation-induced trap $E1$ at $E_c-0.39$ eV observed in Ref. [8]. So for p-type silicon in thermal equilibrium $f^{++} \gg f^{+} \gg f^{0}$ and so we can assign $f^{++} \approx 1$. However it does not mean that the first term in Eq. (4) will dominate. According to the results of Refs. [4–6] the difference between barriers for migration of doubly (E_m^{++}) and singly (E_m^{+}) positively charged self-interstitials is about 0.8–1.2 eV. The Fermi level (E_F) at annealing temperatures in samples under study is near $E_v+0.3$ eV. The ratio (f^{+}/f^{++}) is controlled by the difference $\Delta E=E_I(+/++)-E_F$. The position of the $E_I(+/++)$ level is not determined unambiguously. However we can use the results of theoretical calculations of Ref. [5] which allows us to estimate $\Delta E=0.5–0.6$ eV or evaluate the upper bound for this difference as $\Delta E \le E_c-E_F \approx 0.8$ eV. So we see that $E_m^{++}-E_m^{+} > \Delta E$ and it is possible that the second term in Eq. (4) will be the largest one for our samples.

Let us suggest that the rate of Si_i^{+} disappearance is not as high as compared to processes of charge carrier emission and capture. Then the occupancy number for all charge states will be practically equal to their values in thermal equilibrium. According to Ref. [16] the ratio between f^{+} and f^{++} may be determined as

$$\frac{f_0^{+}}{f_0^{++}} = \frac{c_n^{++}n_0}{e_n^{+}} = \frac{e_p^{++}}{c_p^{+}p_0} \tag{5}$$

where e_p^{++} and e_n^{+} are emission rates of holes by the doubly ionized state and electrons by the singly ionized state of Si_i, respectively, c_p^{+} and c_n^{++} are the capture coefficients of holes and electrons by respective charge states. Equilibrium concentrations of electrons (n_0) and holes (p_0) are related to each other by mass action law: $n_0p_0=n_i^2$, where n_i is intrinsic density of charge carriers.

Suggesting f_0^{++} to be equal to 1 we evaluate f_0^{+} as

$$f_0^{+} = f_0^{++}\frac{N_v}{p_0}\exp\left(-\frac{E_I(+/++)-E_v}{kT}\right) = \theta\exp\left(-\frac{\Delta E_p^{+}}{kT}\right) \tag{6}$$

where N_v is effective density of states in Si valence band, and $\Delta E_p^{+}=E_I(+/++)-E_v$. In this case the annealing rate will be

$$\frac{1}{\tau_I} = \frac{1}{\tau_{I^{+}}} = 4\pi R_I^{+}f_0^{+}D_I^{+} = \theta\exp\left(-\frac{\Delta E_p^{+}}{kT}\right)4\pi R_I^{+}D_I^{+} \tag{7}$$

According to Eq. (7) pre-exponential factor of Si_i annealing will be enhanced by $\theta \sim 10^4–10^5$ times (for $p_0=10^{14}–10^{15}\,cm^{-3}$) and activation energy determined from annealing studies will be

$E_{ann}=\Delta E_p^+ + E_m^+$. Using results of previous theoretical calculations [4–6] we can estimate $E_{ann}=1.1$–1.3 eV.

So, we see that the model, which takes into account a higher diffusivity of the singly ionized self-interstitials can consistently explain the specific features of our experimental data. However, because there are no unambiguous experimental data on electronic properties of self-interstitials in silicon, we cannot unambiguously interpret the determined activation energy for self-interstitial annealing and additional experiments are necessary.

5. Conclusion

Kinetics of interstitial carbon atoms appearance due to the replacement of substitutional carbon by self-interstitials have been studied in silicon n^+–p–p^+ structures irradiated with alpha particles. The value of activation energy of this reaction is found to be of $\sim$1.2–1.3 eV, the pre-exponential factor of annealing constant have an enormously high value ($\sim 10^{14}$–10^{15} s^{-1}) for the diffusion-limited reactions. Suggested explanation of the revealed features of the silicon self-interstitial behavior is based on an assumption that there is a very strong difference in the migration ability of self-interstitials in different charge states.

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