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Primary defect transformations in high-resistivity p-type silicon irradiated with electrons at cryogenic temperatures

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ABSTRACT

It has been revealed that self-interstitials formed under low intensity electron irradiation in high resistivity p-type silicon can be retained frozen up to room temperature. Low thermal mobility of the self-interstitials suggests that Frenkel pairs in silicon can be stable at temperatures of about or higher than 100 K. A broad DLTS peak with activation energy of 0.14–0.17 eV can be identified as related to Frenkel pairs. This peak anneals out at temperatures of 120–140 K. Experimental evidences are presented that becoming more mobile under forward current injection the self-interstitials change their charge state to a less positive one.

1. Introduction

The simplest primary damage event in silicon lattice under bombardment with energetic particles is the formation of a pair of vacancy and self-interstitial atom (V+Si_i or Frenkel pair). When initially formed vacancy and self-interstitial are separated they can be considered as isolated defects. A more complicated primary defect is a pair of two vacancies and interstitials (2V+2Si_i). When separated they can be transformed into isolated divacancy (V_2) and di-interstitial or other vacancy and interstitial containing defects (e.g. V_2+Si_i and separated Si_i, etc.). The existence of the isolated divacancy as primary defect is well known and the threshold energy of its formation is not essentially exceeding that of a stable vacancy [1]. In general, we can conceive any more or less stable primary defect in silicon as a complex of the type mV+$n$$Si_i$ where m, $n \geq 1$ and, in principle, $m \neq n$. So primary defects can be considered as generalized Frenkel defects (GFDs) and it seems that the bombardment of silicon crystals in many available irradiation facilities results in simultaneous production of not a single but a variety of GFDs.

The understanding of primary damage events is one of the fundamental problems of radiation physics of semiconductors. As compared to other primary defects the physical properties of the vacancy in silicon are well documented (see e.g. Ref. [2]) and there is a good consistency between the experimental data on the vacancy obtained in different experimental groups. However, there is no such consensus on properties of self-interstitials and Frenkel defects (pairs) in silicon. In the early 1990s it was assumed that it is impossible to observe Frenkel pairs in silicon [3]. Only several years later some experimental data appeared showing that Frenkel pairs can be observed using DLTS but only after irradiation with light ions and not after irradiation with electrons [4,5]. The method of diffuse X-ray scattering was used in another works where it was suggested that there is a possibility to keep Frenkel defects frozen at relatively high temperatures even after electron irradiation [6,7]. This discrepancy impels other studies of the Frenkel pairs production under electron irradiation.

As pointed out in Ref. [2] electron irradiation has some advantages in studying the processes of primary defect formation: electrons do not produce defect clusters, the electron is not an impurity and it is possible to control the partial number of different types of GFDs by using electrons with different energies.

This work presents experimental results on the studies of the defects formed in p-type silicon under electron irradiation at liquid nitrogen temperature.

2. Experimental details

Two types of silicon structures have been used in our experiments. The first type of samples was produced from high resistivity p-type silicon wafers grown by the MCz method. The electron concentration determined from capacitance–voltage measurements was $2.5–3 \times 10^{12}\,cm^{-3}$. The second type of diodes with a hole concentration of $1.3 \times 10^{13}\,cm^{-3}$ was produced from epitaxial p-Si. Oxygen content in the MCz silicon was about $5 \times 10^{17}\,cm^{-3}$. In the epitaxial diodes oxygen content varies with

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the depth in the range of $5–10 \times 10^{16}\,cm^{-3}$ [8]. Carbon concentration in both the materials was less than $10^{16}\,cm^{-3}$. Both diode structures were produced by Centro Nacional de Microelectrónica (Barcelona, Spain) according to a research plan of the RD50 Collaboration (CERN) [9].

Irradiation with electrons ($E_e = 6\,MeV$) was done at liquid nitrogen temperature (about 78 K). Fluences of electron irradiation were 8×10^{12} and $2.5 \times 10^{13}\,cm^{-2}$ for samples of the first and second type, respectively. Electron beam intensity was equal to $10^{11}\,cm^{-2}\,s^{-1}$. After irradiation at 78 K the samples were transferred to a cryostat for DLTS measurements without heating. To determine the trap parameters we used a least-square procedure which allows simultaneous evaluation of parameters for several peaks [10].

Isochronal annealing studies were performed in the temperature range of 100–400 K. Duration of each annealing step was 15 min.

3. Experimental results and discussion

To observe the DLTS peak related to isolated vacancies at temperatures higher than 78 K, it is necessary to use a rather high rate window [2,4]. However, some traps of interest are annealed at relatively low temperatures. It is therefore also necessary to use a rather low rate window in order to shift the DLTS peaks of these traps to temperatures as low as possible. Therefore to obtain more complete information on the behavior of radiation-induced defects under study we used two rate windows. One high rate window to observe vacancies and one low rate window to observe the other defects. DLTS spectra measured at these two rate windows for a diode prepared from epitaxial silicon are shown in Fig. 1a and b. All DLTS peaks are numbered according to their appearance with measurement temperature.

As expected a vacancy related peak H1 ($T_{peak} = 85\,K$ at $w_r = 950\,s^{-1}$) is observed in the DLTS spectra measured immediately after irradiation. However, due to both low charge carrier concentration and rather high temperature of the peak appearance there is an incomplete occupancy of the $E(0/{++})$ level of the vacancy. Using Hall effect data of Ref. [11] we assessed the occupancy as equal to about $\frac{1}{3}$ in epitaxial and much less in MCz structures. This incomplete occupancy should result in some shift of the H1 trap parameters [12] and explains the deviation of our values of pre-factor and activation energy for the emission rate (see Table 1) from the known results for the vacancy [13,14]. The negative-U nature of the H1 peak was manifested also in the decrease of its height with growing T_{peak} when DLTS spectra are registered with higher rate windows.

An unexpected result is the existence of two sub-peaks H1a and H1b. These sub-peaks are distinctly separated only by annealing. The H1a peak anneals out at temperatures 200–220 K which is characteristic for single vacancies in high resistivity p-Si [2]. The origin of H1b trap is unclear yet. As one can see from the text below a possibility of its formation under our experimental conditions by a reaction Si_i+O_i (see Refs. [4,5]) may be excluded.

Another prominent peak seen in Fig. 1 is peak H3 ($T_{peak} = 113\,K$ at $w_r = 19\,s^{-1}$). This peak is well known and ascribed to ionization of the donor state of the divacancy [2,13,14]. As seen in Fig. 2 the height of H3 falls at annealing temperatures of 300–360 K. It was suggested recently that the component of divacancy peak in p-Si unstable at room temperatures is related to the tri-vacancy [15]. We have found that this component is not annealed out but can be restored by a forward current injection. That is a part of the H3 peak reveals bistable properties similar to two peaks previously observed in neutron irradiated n-Si [16]. As it has been shown in Ref. [17] the two bistable peaks in n-Si are related to two acceptor

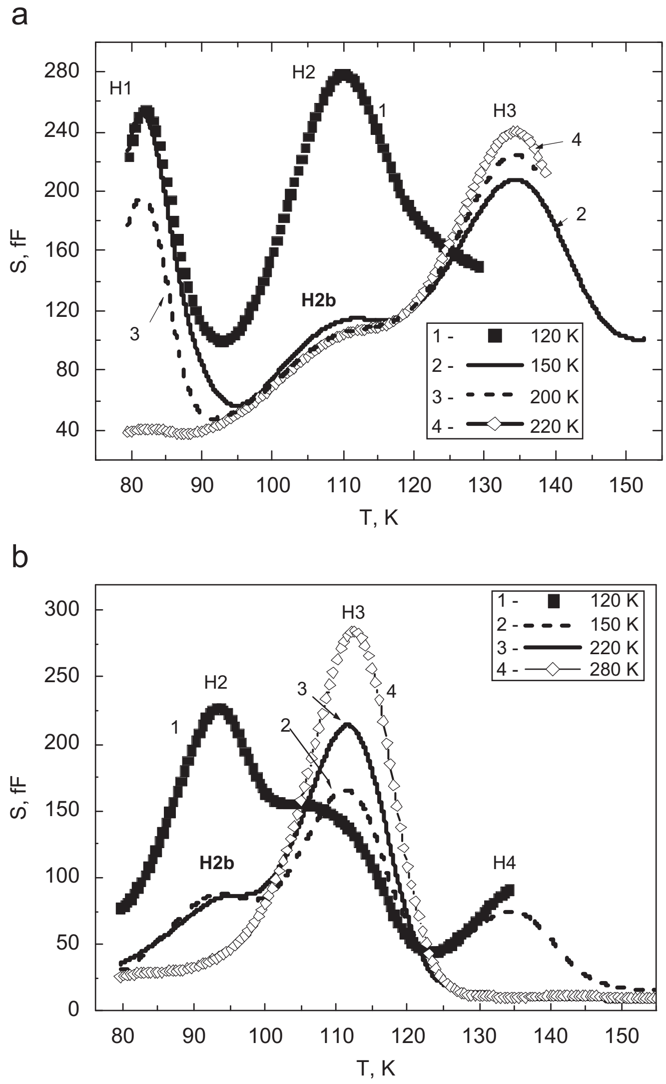

Fig. 1. Evolution of H1–H4 peaks during annealing of epitaxial p-Si irradiated at 78 K. Measurements have been performed at different rate windows: $w_r = 950\,s^{-1}$ (a) and $w_r = 19\,s^{-1}$ (b). Each annealing step was 15 min long. Annealing temperatures are indicated in the figures.

Table 1
Parameters of the main DLTS peaks appearing in p-Si after electron irradiation at LNT and subsequent annealing.

Peak label	Sub-peaks	Pre-factor (s^{-1})	Activation energy (eV)	Peak origin
H1	H1a	2.5×10^8	0.150[a]	V
	H1b	–	–	–
H2	H2a	3.4×10^7	0.139[b]	CFP?
	H2b	3.3×10^6	0.170[c]	–
H3	H3a	4.2×10^5	0.187	V_2
	H3b	3.9×10^5	0.192	V_3
H4	–	3.4×10^7	0.282	–
H5	–	1.8×10^7	0.292	C_i
H6	H6a	2.4×10^7	0.364	$C_iO_i^*$
	H6b	3.1×10^6	0.352	C_iO_i

[a] This value shifted due to partial occupancy of the $E(0/{++})$ level of vacancy [12].
[b] Main component of H2a peak.
[c] A preliminary value.

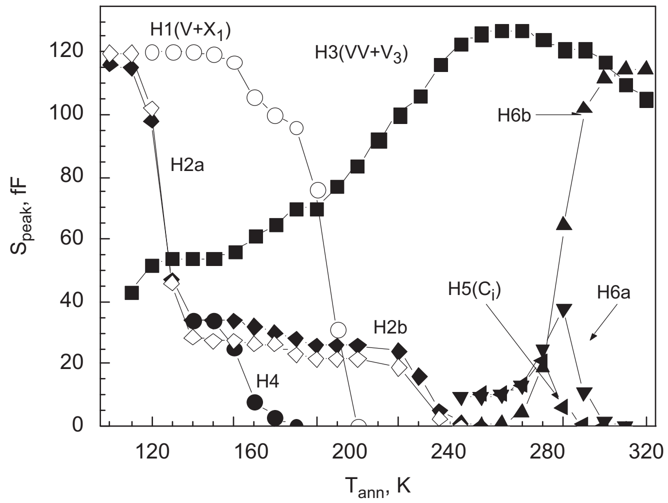

Fig. 2. Evolution of the heights of the main DLTS peaks observed in diodes irradiated at 78 K and annealed at 100–350 K with temperature step 10 K. The annealing duration at each temperature was 15 min. Filled and empty symbols are for the MCz and epitaxial diodes, respectively.

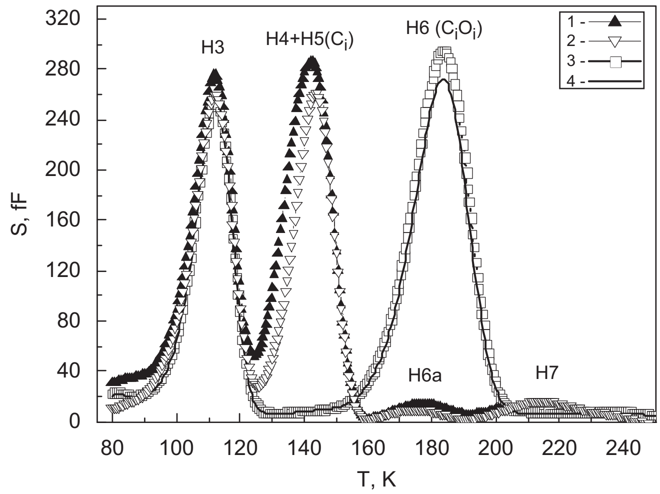

Fig. 3. Comparison of DLTS spectra measured after irradiation and forward current injection at 78 K (1) and after subsequent annealing steps at 200 (2) and 360 K (3) of the same epitaxial diode. The solid line (4) another diode which underwent only a sequence of thermal annealing steps up to 360 K.

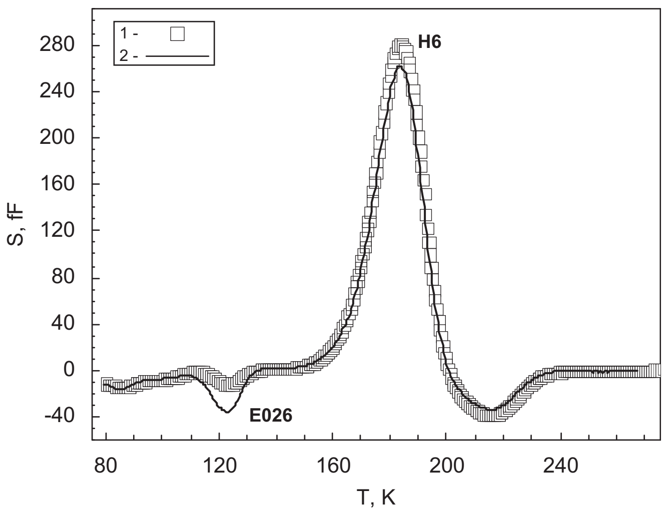

Fig. 4. DLTS spectra measured using minority carrier injection for diodes after annealing at 360 K. One of them was subjected to forward current injection at 78 K immediately after irradiation (points). Another was annealed up to 360 K only thermally (line).

states of the tri-vacancy. This is the reason why we suggest that the bistable H3b peak is related to the donor state of the tri-vacancy. The difference between signatures of V_2 and V_3 is very small and can be revealed by using cycling of thermal annealing and forward current injection procedures.

The H1 and H3 peaks can serve as reference points to describe the characteristics of other traps in the diodes. It is useful to describe the position of any new peak relatively to these peaks. Further well known peaks are H5 and H6b. H5 is related to interstitial carbon (C_i) and appears in epitaxial diodes after thermal annealing at higher temperatures ($T_{ann} \geq 300$ K) or after forward current injection at 78 K (see Fig. 3). H6b is related to the interstitial carbon–interstitial oxygen complex (C_iO_i) and achieved its final height after annealing at 350–360 K (Figs. 2 and 3a). The peak labeled as H6a is related to a precursor of the interstitial carbon–interstitial oxygen complex ($C_iO_i^*$) [8,10]. The appearance of carbon related defects can be described by the following reactions. C_i appears by the Watkins replacement mechanism: $Si_i + C_s \rightarrow C_i$. And C_iO_i appears by two ways: (1) $C_i + O_i \rightarrow C_iO_i$ and (2) $C_i + O_i \rightarrow C_iO_i^* \rightarrow C_iO_i$.

Both, H5 and H6, appear only when self-interstitial silicon atoms become mobile. As seen from Fig. 1b (curve 4) there is no H5 trap in epitaxial diodes even after annealing at 280 K. In MCz diodes we observe some background concentration of traps with their T_{peak} similar to those for H5 and H6a. The origin of these background traps is unclear yet. However, it is clear from Fig. 2 that the essential growth of the defects related to interstitial carbon starts at about 300 K. It means that Si_i are immobile at lower temperatures.

Taking into account that vacancies and self-interstitials are immobile at $T < 200$ K it is reasonable to search for Frenkel pairs among the defects unstable at 200 K. Two possible candidates are the H2 and H4 traps.

The height of the H2 peak is of the same order as H1 and H6. This peak is rather broad and it is possible to distinguish at least three components within the peak. Two components are stable only till 120 K upon thermal anneal and the third one anneals at temperatures higher than 240 K. However, all of them are annealed by forward current injection at 78 K (Fig. 3, curve 1). This sensitivity to injection is similar to properties of V and Si_i.

In contrast to the behavior of the H2 trap the height of the H4 peak does not decrease after injection at 78 K. In contrary, it even shows a small growth. This peak is stable till 140 K. However, the fact that the peak appears in the DLTS spectra at rather high temperatures only does not allow us to say what was the concentration of the H4 trap immediately after irradiation. It is possible that the H4 peak is a result of other primary defect transformations.

The comparison with previous studies shows that some of our data are consistent with those obtained by other authors and some of them are different. First of all we can say that there is qualitative consistency with the results of other groups [2,4,5]. Those are the properties of the isolated vacancy [2], the immobility of the Si self-interstitials in p-type Si at $T \leq 300$ K, the relatively high concentration of the H2 trap and its identification as a primary defect [4,5]. Traps similar to H2 (H2a and H2b) were observed also in Ref. [14] where irradiation with 2 MeV electrons had been used (it was labeled in Ref. [14] as AA12). The lower energy of bombardment particles resulted in relatively low concentrations of the divacancy and AA12.

Due to its high sensitivity to injection of charge carries our H2 defects seemingly could not be observed in experiments using X-ray diffraction [6,7]. More probable it was the H4 trap.

As seen in Fig. 3 (curves 3 and 4) the H3 peaks are of the same heights for both diodes annealed with preliminary forward current injection and without any injection. However, there is a distinct difference between respective heights of the H6 peak. This difference is seen more clearly when DLTS spectra were measured with forward filling pulse (Fig. 4). Some difference observed also for the E026 peak which was identified earlier [18] as related to complex B_iO_i. It means that the more self-interstitials become mobile under forward current injection the less is their capture cross section by substitutional boron (B_s). As subtitutional boron is negatively charged at 78 K it would be reasonable to suggest that this decrease of the trapping probability results from a reduction of Coulomb attraction between Si_i and B_s.

4. Conclusions

The use of high resistivity p-Si allows us to observe several primary defects frozen after electron irradiation at 78 K. We show that electron irradiation can be used to observe Frenkel pairs and to obtain additional information on the formation and properties of not only isolated vacancies and self-interstitials but other primary defects in silicon.

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