

Room-temperature annealing of vacancy-type defect in high-purity n -type Si

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Electron-irradiated $p^+-n^-n^+$ diodes produced from low-doped high-purity Si wafers were found, by deep-level transient spectroscopy (DLTS), to have a prominent defect, labeled $E4$, with an energy level 0.37 eV below the conduction-band edge and a concentration of $\sim \frac{1}{4}$ relative to the divacancy. The samples were kept at room temperature, and the $E4$ concentration was seen to reduce to half during five weeks. Annealing data revealed a similar peak $E5$ overlapping that of the single-negatively charged divacancy and showing a one-to-one proportionality with $E4$. $E4$ and $E5$ arise most likely from a vacancy-type defect and a tentative assignment to a planar tetravacancy is put forward.

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Irradiation of Si with high-energy particles causes formation of intrinsic defects, which constitute charge carrier traps that reduce the concentration of free charge carriers. In most applications today a change in the charge-carrier concentration is undesired. One such application is the use of Si detectors in the Large Hadron Collider (LHC) and the planned Super LHC at CERN. With total doses up to 10^{15} – 10^{16} cm $^{-2}$, the generation of defects trapping charge carriers is of major concern, as this trapping is regarded to set the ultimate limit for operation at very high radiation fluences.¹ The radiation tolerance of Si is, therefore, of great interest, and considerable effort has been put into a series of investigations (e.g., report of the CERN RD50 collaboration² and references therein).

At the same time, p - n structures fabricated from high-purity detector-grade Si represent an almost ideal model system for studies of fundamental defects. For example, using such structures, divacancy (V_2) migration and interaction with impurities has been studied in detail,^{3,4} and electronic properties of the divacancy-oxygen (V_2O) complex have been investigated.^{5,6} In this contribution, we have observed two defect states, presumably of acceptor type, which display a limited stability at room temperature (RT) and can be a fundamental vacancy-type complex.

Two types of $p^+-n^-n^+$ high-purity Si diodes have been investigated. One type is produced from magnetic-Czochralski (MCz) wafers with a phosphorus doping of 5×10^{12} cm $^{-3}$, while the other is produced from standard-float-zone (STFZ) wafers with a doping of 4×10^{12} cm $^{-3}$. For the MCz samples the oxygen and carbon concentrations are found, by secondary-ion mass spectrometry (SIMS), to be 0.5 – 1×10^{18} cm $^{-3}$ and $\leq 10^{16}$ cm $^{-3}$, respectively. For the STFZ samples, the bulk concentration of oxygen is $< 5 \times 10^{15}$ cm $^{-3}$; the carbon concentration is 2 – 4×10^{16} cm $^{-3}$. Aluminum was used as contact metal. The samples were kept at RT ($\sim 23^\circ\text{C}$) after they had all been irradiated at RT with 6-MeV electrons to a dose of 5×10^{12} cm $^{-2}$.

The setup used for the deep-level transient spectroscopy (DLTS) measurements, based on a HP 4280A capacitance

meter, is a refined version of one described elsewhere.⁷ Both a lock-in-type weighting function and a GS4 weighting function⁸ were used to extract the DLTS signal. Subsequently, the concentration, energy level position and apparent capture cross section of the electron traps were derived.

Figure 1 shows the DLTS spectra measured for MCz and STFZ samples 175 and 28 h after the electron irradiation, respectively. Alongside the peaks of the vacancy-oxygen (VO), $V_2(=/-)$ and $V_2(-/0)$ levels is also the peak $E4$ which has a similar amplitude in the two materials. The STFZ spectrum is multiplied by a factor of 1.05 to remove a 5% difference in the peak amplitudes relative to the MCz sample, well within the irradiation dose accuracy. After 2036 h at RT, the $E4$ peak disappears and a decrease in the amplitude of $V_2(-/0)$ is observed. It will later be shown more clearly that

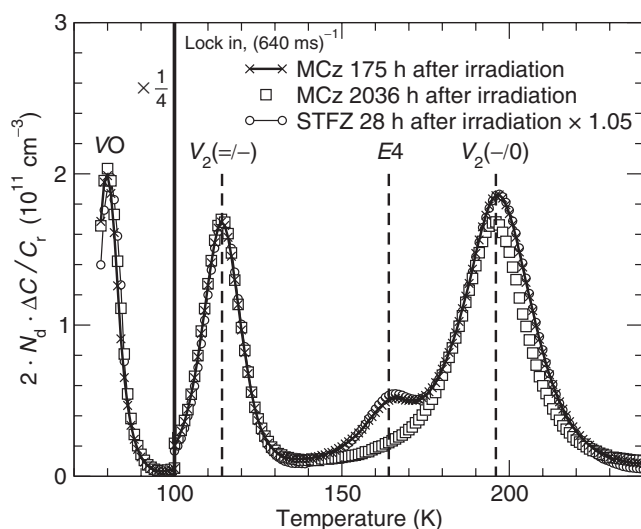


FIG. 1. DLTS spectra of MCz and STFZ samples obtained 175 and 28 h after the electron irradiation, respectively, compared with the spectrum of the MCz sample annealed 2036 h at RT. The $(640 \text{ ms})^{-1}$ rate window of the lock-in weighting function is used and the low-temperature end of the spectrum is reduced by a factor of 4.

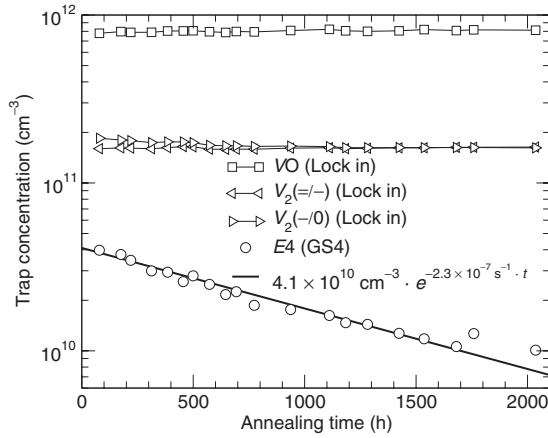


FIG. 2. The concentration of the four defect configurations from Fig. 1 after different annealing times at RT. The concentration of $E4$ is deduced using the GS4 weighting function and fitted by an exponential curve (t is the annealing time). The other lines are guides to the eye.

there is also a corresponding increase in the amplitude of VO.

The trap concentration N_t is deduced from the DLTS spectra using the expression $N_t = 2N_d \Delta C / C_r$ at the peak maxima in the spectra.⁹ This expression neglects a $\sim 10\%$ reduction due to the depletion depth at zero bias and the so-called lambda correction.

In Fig. 2, the evolution of the amplitudes of the defect peaks in the MCz sample is shown. The time dependence of the $E4$ concentration is fitted, by the method of least mean squares, by an exponential curve. The data points have a slight upwards curvature compared to the exponential fit. This curvature can be explained by a nonzero baseline in the spectra causing an offset of $\sim 1 \times 10^{10} \text{ cm}^{-3}$.

Given the deduced annealing rate of $E4$ of $2.3 \times 10^{-7} \text{ s}^{-1}$, one can estimate that the activation energy is in the range 0.9–1.2 eV, depending on the prefactor (typically 10^9 – 10^{13} s^{-1}).

Figure 3 shows the change in amplitude of the VO, $V_2(=/-)$ and $V_2(-/0)$ peaks as a function of the loss in amplitude of the $E4$ peak. It can be seen that the amplitude of the $V_2(-/0)$ peak is reduced by about the same amount as that of the $E4$ peak throughout the investigation. Although the large amplitude of the VO peak causes some scatter, the VO concentration can be seen to increase with an amount similar to the loss of $E4$. No significant change occurs for $V_2(=/-)$.

Figure 4 shows the temperature interval 100–280 K of the DLTS spectra measured 78, 499, and 1111 h after the irradiation subtracted by the spectrum measured after 2036 h. The data suggest that the reason for the one-to-one proportionality between $E4$ and $V_2(-/0)$, shown in Fig. 3, is a peak overlapping with $V_2(-/0)$. This peak, labeled $E5$, has an amplitude identical, within the experimental accuracy, to that of $E4$ and anneals at the same rate as $E4$. This observation suggests that the $E4$ and $E5$ peaks are due to two different charge states of the same defect.

The signatures of $E4$ and $E5$ have been deduced from

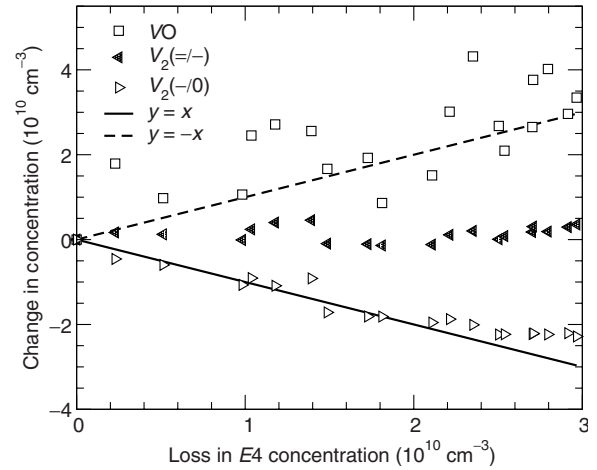


FIG. 3. The data from Fig. 2 rearranged to show defect-concentration changes as a function of the loss in the concentration of $E4$. The change of $E4$ is shown as the line $y = -x$. The lost concentration of $E4$ is shown as $y = x$.

spectrum differences such as the ones in Fig. 4; an average of these gives for $E4$ an energy position at 0.37 eV below the conduction-band edge and an apparent capture cross section of $1 \times 10^{-14} \text{ cm}^2$, and the corresponding values for $E5$ are 0.45 eV and $3 \times 10^{-15} \text{ cm}^2$. The values for the apparent capture cross section are of the same order of magnitude, suggesting significant influence by entropy factors and/or temperature-dependent cross sections, similar to that found for the different charge states of V_2 .¹⁰

The presence and annealing of $E4$ at RT is seen with the same concentration and rate also in STFZ samples, diffusion-oxygenated FZ (DOFZ) samples and hydrogenated samples. Given the different oxygen and carbon concentrations in MCz and STFZ material, this indicates a fundamental intrinsic nature of $E4$.

$E4$ may be assumed to originate from the previously observed substitutional-phosphorus–interstitial-carbon (P_sC_i)

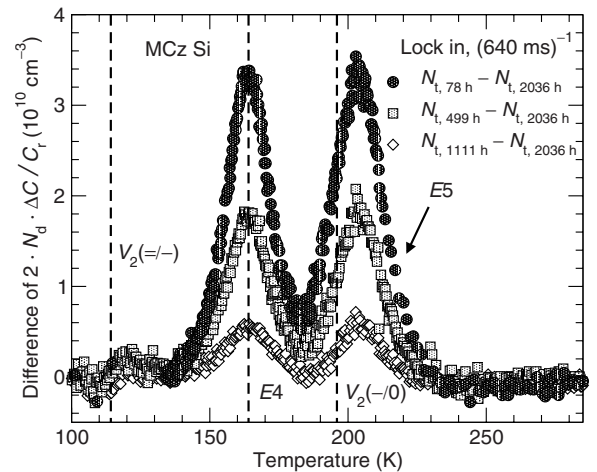


FIG. 4. The three DLTS spectra calculated from the capacitance transients measured after 78, 499, and 1111 h subtracted by the transients measured after 2036 h, respectively. The positions of the $V_2(=/-)$, $E4$, and $V_2(-/0)$ peaks are marked for comparison with Fig. 1.

center which has a similar DLTS signature and is unstable at RT.¹¹ The samples investigated in the present work, however, have too low phosphorus concentration relative to the oxygen concentration to form a measurable concentration of P_sC_i . In Ref. 11, for instance, no P_sC_i is detected when the oxygen-to-phosphorus ratio is 2×10^3 , as most of the C_i is then captured by oxygen. For the STFZ material in the present work this ratio is $\approx 1.3 \times 10^3$, while for the MCz material it is $\sim 10^5$. The concentration of $E4$ in the MCz and STFZ materials is, nevertheless, similar. Hence, an assignment of $E4$ to P_sC_i is excluded. Indeed, it seems $E4$ is not related to carbon at all, as the carbon-capturing defect needs to have a high concentration to compete with the formation of interstitial-carbon-interstitial-oxygen (C_iO_i) pairs. However, the $E4$ generation rates are similar in the MCz and STFZ materials despite the very different carbon-to-oxygen ratios.

In 7-MeV proton-irradiated DOFZ samples the generation of $E4$ is enhanced relative to that of VO and V_2 in comparison with the present results for 6-MeV electron irradiation.¹² In Ref. 12 $E4$ (and most likely $E5$) disappears rapidly and is below the detection limit after 15 min at 50°C. As proton irradiation causes a higher density of intrinsic defects compared to electron irradiation, the enhanced generation of the $E4$ and $E5$ levels in proton-irradiated samples indicates that these levels arise from a higher-order center larger than, for instance, a divacancy. This speculation is further supported by the small difference in the energy-level positions of the, presumably, two different charge states. Indeed, as the distance between the dangling bonds is increased in a larger center, the Coulomb repulsion and thus the difference in binding energy between the two trapped electrons decreases.

It should be mentioned that peaks similar to $E4$ and $E5$ have been observed also in neutron-irradiated Si.^{13–15} However, these reported peaks do not exhibit a one-to-one ratio in the amplitudes,¹³ in contrast to what is shown in Fig. 4. The absence of a one-to-one ratio between $E4$ and $E5$ in neutron-

irradiated Si does not contradict the identification of the levels as two charge states of the same defect, but indirectly supports it. This difference in peak amplitudes can readily be explained by incomplete occupation of the shallower state, similarly to the effect observed for $V_2(=/-)$ in neutron-irradiated Si.¹⁴

The correlation between the growth of VO and the loss of $E4$ and $E5$ indicates that $E4$ and $E5$ are due to a vacancy-related defect. This, together with the indication that $E4$ and $E5$ arise from a higher-order defect center, may suggest an assignment to the {110}-planar tetravacancy chain (V_4) observed by Lee and Corbett in neutron-irradiated Si.¹⁶ This is also consistent with the speculations of Watts *et al.*¹⁷ In this context, it should be pointed out that the maximum energy transfer of a 6-MeV electron to a Si atom is of the order of a few keV and despite being rather rare events, defect clusters such as V_4 (or even higher order) can be formed by recoiling Si atoms having sufficient energy. The planar V_4 exhibits a rather limited temperature stability which may be consistent with that of $E4$ and $E5$, but further studies must be pursued for a more definite assignment.

In summary, a defect with a level 0.37 eV below the conduction-band edge is found to arise when high-purity n -type Si is electron irradiated. The defect anneals exponentially at RT and has a half-life of about five weeks. Another defect level, with the same concentration and temperature stability as the one at 0.37 eV, is found 0.45 eV below the conduction-band edge. These two levels are presumably due to two different charge states of the same defect. As the two defect levels anneal out, an equal increase in the VO concentration occurs. A tentative identification of $E4$ and $E5$ as two charge states of the {110}-planar tetravacancy chain is put forward.

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