

Defects in p-type Cz-silicon irradiated at elevated temperatures

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P-type Czochralski grown (Cz) silicon samples have been irradiated at room temperature (RT), 350, and 450 °C with 1.8 MeV protons to doses of 2×10^{12} and $1 \times 10^{13} \text{ cm}^{-2}$ and analyzed by deep level transient spectroscopy (DLTS). The generation rate of interstitial carbon–interstitial oxygen (C_iO_i) increases with the irradiation temperature, suggesting less efficient annihilation of self-interstitials and mono-vacancies at elevated temperature. A defect located at $\sim E_v + 0.39 \text{ eV}$ (E_v denotes the valence band edge) appears in the sample irradiated at 450 °C and also emerges at the expense of C_iO_i center in the sample

irradiated at RT and subsequently heat-treated above 400 °C. The amplitude of this level is enhanced in the sample irradiated at 450 °C. By comparing the annealing behavior found by photoluminescence (PL) measurements and reported theoretical predictions, the $\sim E_v + 0.39 \text{ eV}$ level is tentatively assigned to the interstitial carbon–oxygen dimer (C_iO_{2i}). In addition, other levels at $\sim E_v + 0.34 \text{ eV}$ and $\sim E_v + 0.58 \text{ eV}$ are observed in samples irradiated at 450 °C and RT with heat treatment in the range of 400–500 °C.

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1 Introduction Electrically active point defects can serve as effective recombination centers and reduce the charge carrier lifetime in Si devices [1–3]. The most prominent impurities in Cz-Si are interstitial oxygen (O_i) and substitutional carbon (C_s). O_i is known to be mobile at elevated temperatures and form clusters. The oxygen dimer or two oxygen atoms together is the first of such process. It is widely believed that the oxygen dimer (O_{2i}) [4,5] plays a crucial role in light induced degradation (LID) of Si solar cells although the complex causing LID has not been experimentally identified [6,7]. Thus, the understanding O_{2i} related complexes are highly important.

The most common electrically active defects in p-type Cz-Si found after room temperature (RT) irradiation are the divacancy (V_2), interstitial carbon (C_i), interstitial boron–interstitial oxygen (B_iO_i) and vacancy–oxygen (VO) [8–10]. C_i is mobile around RT and form a complex with O_i , the C_iO_i center, after a few hours. A subsequent annealing after the irradiation at RT causes new defect complexes, such as impurity related defects, but also annealing of low-order irradiation induced defects. Most of the irradiation induced defects anneal out below 400 °C, while some carbon re-

lated defects have a slightly higher thermal stability i.e. $\geq 400 \text{ °C}$ [10,11].

The formation of the so-called P-line has been observed by photoluminescence (PL) spectra in electron irradiated Cz-Si upon annealing of the interstitial carbon–interstitial oxygen (C_iO_i) center at 400–450 °C [12,13]. Moreover, it has also been shown that the P-line appears only in carbon rich material and it is identified as a carbon–oxygen center [12–14], but the electrical activity of this center is unknown. DLTS studies of high temperature irradiation induced defects in Si are scarce. More information about defects with high thermal stability can be extracted by irradiating at elevated temperatures, where specific defect complexes, like B_iO_i , are no longer stable.

In the present study, we have performed a DLTS analysis of the defect–impurity complexes in boron doped p-type Cz-Si samples after irradiation at RT, 350 and 450 °C with subsequent heat treatment. The formation of a new defect level at $\sim E_v + 0.39 \text{ eV}$, close in energy position with that of C_iO_i , has been revealed in the temperature range 400–450 °C, and it is tentatively assigned to the interstitial carbon–oxygen dimer (C_iO_{2i}).

2 Experimental Two sets of samples were used, n^+p diodes and Schottky diodes. The n^+p diodes were prepared on boron doped Cz-Si wafers with resistivity of $\sim 6 \Omega\text{cm}$. First, the wafers were dry oxidized at 1100°C for 3 hours to grow a 250 nm thick SiO_2 layer. Standard photolithography and wet etching using buffered oxide etch (BOE) were then applied to open holes with a diameter of 200–2000 μm in selected areas. The n^+ layer was formed by in-diffusion of phosphorous (P) from gas phase in a quartz tube. Aluminum (Al) Ohmic contacts were prepared by thermal evaporation on the front side (n^+ side) and silver paste was used as contact on the back side after removal of the SiO_2 layers by BOE. The Schottky diodes were formed on boron doped Si-wafers with a resistivity of $\sim 13 \Omega\text{cm}$ which were prepared by dipping the samples in HF solution (HF , H_2O , 1:50) and further cleaned in RCA3 (H_2O , HCl , H_2O_2 , 5:1:1, at 80°C). Schottky contacts were then realized by thermal evaporation of Al through a metal mask on the front-surface and Ohmic contacts were achieved by applying silver-paste on the back-side. The samples were irradiated with 1.8 MeV protons to doses in the range of 2×10^{12} – $1 \times 10^{13} \text{ cm}^{-2}$ and the temperature during the irradiation was RT, 350°C and 450°C . Irradiation details of the samples are given in Table 1. After the irradiation at 450°C , cooling of the samples took about 120 and 480 min to reach 250°C and RT, respectively. Isochronal annealing (30 min duration) was carried out for temperatures in the range of 300 – 500°C .

The oxygen and carbon concentration in the samples were $(4\text{--}7) \times 10^{17} \text{ cm}^{-3}$ and $\leq 2 \times 10^{16} \text{ cm}^{-3}$, respectively, as determined by secondary ion mass spectrometry (SIMS). The DLTS measurements were carried out by employing a refined version of the set-up described in Ref. [15] with forward bias of 0 V during the filling pulse. The reverse bias quiescent voltage was kept at 10 V with a filling pulse width of 50 ms. The DLTS signal was extracted using a lock-in weighting function with six different rate windows in the range of $(20 \text{ ms})^{-1}$ – $(640 \text{ ms})^{-1}$.

Table 1 Irradiation details of the samples used in this study.

Sample label	Resistivity (Ωcm)	Irradiation temperature	Dose (cm^{-2})
A	6	RT	2×10^{12}
B	6	350°C	2×10^{12}
C	13	RT	10^{13}
D	13	450°C	10^{13}

3 Results and discussion

3.1 Irradiation at RT and 350°C Figure 1 shows the DLTS spectra of samples A and B, and the parameters of the levels observed are listed in Table 2. The dominant levels arise from the donor state of V_2 ($+0$) and C_iO_i . The heat-treatment of sample A at 300°C results in the annealing of V_2 and the formation of a new defect level close to that of V_2 ($+0$). This new level consists of two contribu-

tions with energy positions at $\sim E_v + 0.23 \text{ eV}$ and $\sim E_v + 0.24 \text{ eV}$. The former one is consistent with an assignment to the donor state of divacancy-oxygen pair (V_2O ($+0$)) [16,17] while the latter is tentatively identified as trivacancy-oxygen (V_3O ($+0$)) [17], although other identifications, for instance V_2O_2 ($+0$), cannot be completely ruled out. Parameters for the overlapping levels are deduced by fitting of the DLTS spectra. The amplitude of the V_2O ($+0$)+ V_3O ($+0$) level decreases after the heat treatment at 350°C . The level related to V_2O ($+0$)+ V_3O ($+0$) is also present in the hot-irradiated sample B.

The amplitude of the C_iO_i level in sample A is stable up to 300°C and decreases then at 350°C , consistent with earlier reports and the annealing kinetics of C_iO_i [11]. Interestingly, the generation rate i.e., the trap concentration divided by proton dose, of C_iO_i increases by about a factor of 3 when the irradiation temperature increases from RT to 350°C , suggesting less efficient correlated annihilation of self-interstitials and mono-vacancies at elevated temperatures [19].

A new level at $\sim E_v + 0.29 \text{ eV}$, attributed to interstitial boron-substitutional carbon (B_iC_s) [10], appears in sample A after annealing at 300°C . Further annealing at 350°C results in the disappearance of B_iC_s , consistent with previous data in the literature [10]. This level is not observed in sample B, corroborating an unstable complex at 350°C .

In Ref. [17], a defect level was reported at $E_v + 0.087 \text{ eV}$ after RT irradiation and annealing at 300°C and an identification as V_2O ($2+/+$) was put forward. Indeed, Fig. 1 unveils a defect, labeled H1, with an energy level at $\sim E_v + 0.09 \text{ eV}$ but with a low concentration relative to V_2 (V_2O) and V_3O , in accordance with the observations in Ref. [18]. The amplitude of the defect is below the detection limit after annealing at 350°C . The defect H1 is also observed in sample B and the amplitude of the defect is almost equal to sample A with heat-treated at 300°C . Accordingly, these data do not support an assignment of H1 to V_2O ($2+/+$).

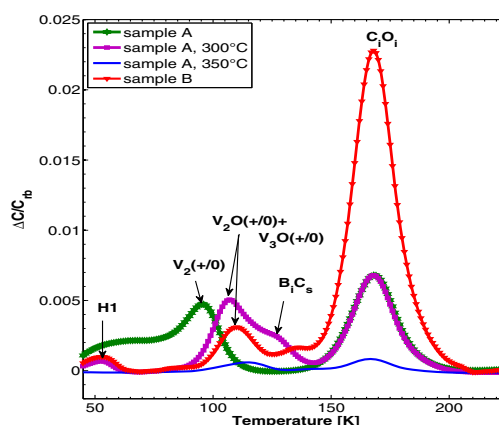


Figure 1 DLTS spectra of samples A and B. A rate window of $(640 \text{ ms})^{-1}$ was used.

3.2 Irradiation at RT and 450 °C A comparison of the DLTS spectra for sample C and D is demonstrated in Fig. 2. As for sample A, the dominant levels in sample C are $V_2 (+/0)$ and C_iO_i .

The V_2 center is absent after the annealing of sample C at 400 °C and is not observed in sample D, which is consistent with earlier reports [17,18].

The amplitude of the C_iO_i level decreases in sample C as the annealing temperature rises to 400 °C. The C_iO_i center is also observed in sample D but below the detection limit after the subsequent heat treatment at 475 °C.

A new level H4 with an energy position at $\sim E_v + 0.39$ eV emerged in sample C, which is close in energy position and overlaps with the C_iO_i level, after the heat treatment at 400 °C. This level is also observed in sample D with increased concentration, as shown in Fig 2, and the amplitude of the level decreases after annealing at 475 °C.

Two other levels H3 and H5 appear in sample C after the heat treatment at 400 °C, but are observed in sample D only after annealing at 475 °C. One can observe several minor peaks at temperatures <130 K, these peaks are outside of the scope of the present work and will be studied in detail in future investigations.

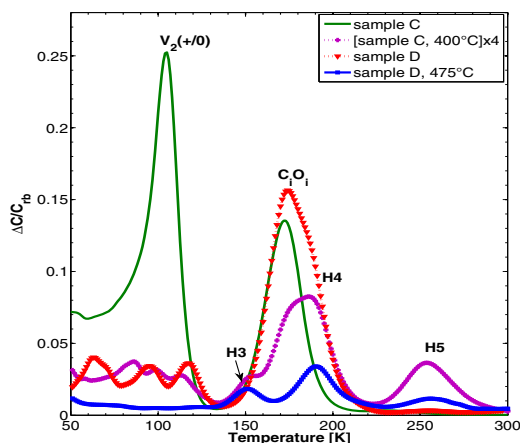


Figure 2 Comparison of DLTS spectra for samples C and D. A rate window of $(640 \text{ ms})^{-1}$ was used.

DLTS spectra of sample C after isochronal annealing in the range of 400–500 °C is depicted in Fig. 3. The amplitude of the C_iO_i level decreases after the annealing at 400 °C and is below the detection limit after about 450 °C.

The level H4 emerges in sample C at 400 °C, increases up to 450 °C annealing and then decreases after the treatment at 475–500 °C.

As mentioned earlier, H3 and H5 appear at 400 °C. The amplitude of H3 increases then up to 475 °C and thereafter decreases at 500 °C while the amplitude of the level H5 increases up to 450 °C and then decreases to low levels at about 475–500 °C, as shown in Fig. 3. It can be speculated that C_i , released from C_iO_i , is involved in the formation of

H3 and H5. Moreover, from the capture cross section (CCS) measurements on sample D after heat treatment at 475 °C (data not included), it is found that the H5 peak consists of two levels with CCS of $\sim 10^{-15}$ and $\sim 10^{-16} \text{ cm}^2$.

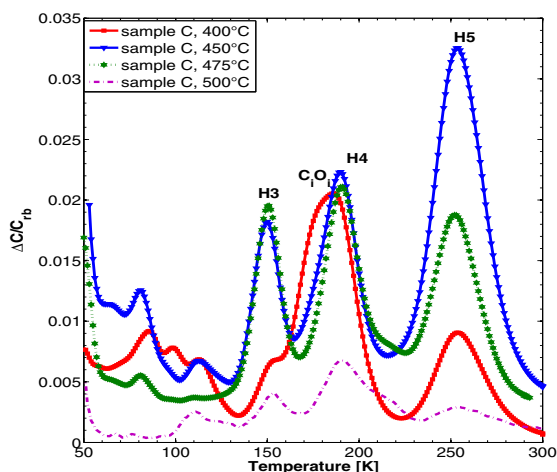
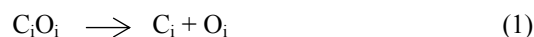


Figure 3 DLTS spectra of p-type Cz-samples C and subsequent annealing in the range of 400–500 °C. A rate window of $(640 \text{ ms})^{-1}$ was used.

Table 2 Defects labels and their parameters: energy level position and apparent capture cross section.

Defect label	Energy level (eV)	Apparent capture cross section (cm^2)
H1	$E_v + 0.09$	10^{-16}
$V_2 (+/0)$	$E_v + 0.19$	10^{-16}
$V_2O (+/0)$	$E_v + 0.23$	10^{-15}
$V_3O (+/0)$	$E_v + 0.24$	10^{-15}
B_iC_s	$E_v + 0.27$	10^{-15}
H3	$E_v + 0.34$	10^{-16}
C_iO_i	$E_v + 0.36$	10^{-15}
H4	$E_v + 0.39$	10^{-15}
H5	$E_v + 0.58$	10^{-15} and 10^{-16}

3.2.1 H4; $E_v + 0.39$ eV level When C_iO_i dissociates, its constituents may react with other defects or impurities. As oxygen is the most abundant impurity, a reaction with the oxygen dimer becomes a likely scenario in the temperature range 400–450 °C.



In reaction (1), C_iO_i dissociates into C_i and O_i , and these C_i 's can be trapped by O_{2i} 's, which are present in oxygen rich materials at concentrations in the range of 10^{14} – 10^{15}

cm^{-3} , to form C_iO_{2i} complex. Here, it should be noted that the concentration of H4 is enhanced in sample D by ~ 4 – 5 times compared to that of sample C annealed at 450°C . It has been shown that irradiation at elevated temperatures enhances the O_{2i} concentration [20,21] which is a likely cause for the large amplitude of H4 in sample D.

Recently, a defect signature similar to H4 was observed in epi-Si electron irradiated at RT and annealed at of 425 – 450°C [23]. Using PL analysis, a similar of annealing behavior has also been observed for the so-called P-line in electron irradiated Cz-Si samples upon annealing of the C_iO_i center [12–14]. The P-line (positioned at 0.767 eV) appears after heat treatment at 400 – 450°C and disappears in the range 500 – 550°C . Since the P-line occurs only in carbon-rich material, it has previously been identified as a carbon–oxygen related center [12–14]. Moreover, results by Ewels *et al.*, [22] suggest that a donor level with position at $E_v+0.39\text{ eV}$ is related to C_iO_{2i} using the local spin density functional super cell code AIMPRO. An additional O_i atom displaces the energy level of C_i related complex upward, in the series C_i , C_iO_i , C_iO_{2i} where the donor levels are found at $\sim E_v+0.28$, $\sim E_v+0.34$, $\sim E_v+0.39\text{ eV}$, respectively [22].

In summary, irradiation induced electrically active defects with high thermal stability in p-type Cz-Si have been studied. The generation rate of C_iO_i increases when increasing the irradiation temperature from RT to 350°C , suggesting less efficient annihilation between self-interstitials and mono-vacancies at elevated temperature. At temperatures around 400°C , annealing of C_iO_i coincides with the growth of three new defect levels. By comparing the annealing behavior of the H4 level at $\sim E_v+0.39\text{ eV}$ with the previously identified P-line (0.767 eV) by PL measurements, we tentatively assign H4 to the level to C_iO_{2i} , also supported by theoretical predictions. The concentration of H4 is enhanced in the sample irradiated at 450°C , consistent with an enhanced concentration of O_{2i} after hot irradiation.

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