

# Formation of donor and acceptor states of the divacancy–oxygen centre in p-type Cz-silicon

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## Abstract

The formation of the divacancy–oxygen centre ( $V_2O$ ) in p-type Czochralski-grown silicon has been investigated by means of deep level transient spectroscopy (DLTS). The donor state (+/0) of  $V_2O$  is located at  $\sim E_v + 0.23$  eV ( $E_v$  denotes the valence band edge) and emerges during heat treatment above 200 °C at the expense of the divacancy centre ( $V_2$ ). A concurrent transition takes place between the single-acceptor states of  $V_2$  and  $V_2O$ , as unveiled by the injection of electrons through optical excitation during the trap filling sequence of the DLTS measurements. Further, a defect with an energy level at  $\sim E_v + 0.09$  eV evolves in close correlation with the growth of  $V_2O$  but at a factor of  $\sim 5$ – $6$  lower in concentration. In the literature, the  $E_v + 0.09$  eV level has previously been attributed to a double-donor state of  $V_2O$  but this assignment can be ruled out by the present data favouring a complex formed between migrating  $V_2$  centres and a competing interstitial oxygen trap. In addition, a level at  $\sim E_v + 0.24$  eV occurs also during the heat treatment above 200 °C and is tentatively assigned to the trivacancy–oxygen centre ( $V_3O$ ).

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Vacancy-related defects influence the electrical and optical properties of Si materials and can serve as effective recombination centres, reducing the minority charge carrier lifetime in devices [1, 2]. In solar cell fabrication, it has recently been shown that divacancies ( $V_2$ ) can be introduced in a significant concentration during heat treatment, e.g., for doping, and affect the conversion efficiency [3]. The  $V_2$  centre is the most prominent intrinsic point defect stable at room temperature (RT) and is strongly enhanced in concentration after particle irradiation and ion implantation.  $V_2$  has four charge states: positive, neutral, singly negative and doubly negative [4]. The corresponding levels occur at about  $\sim E_v + 0.19$  eV,  $\sim E_c - 0.42$  eV and  $\sim E_c - 0.23$  eV, and are attributed to positive (+/0), negative (−/0) and doubly negative (=/−) transitions of  $V_2$ , respectively ( $E_v$  and  $E_c$  denote the valence and conduction band edge, respectively). In p-type silicon, only  $V_2$  (+/0) can be detected by means of deep level

transient spectroscopy (DLTS), or minority carrier transient spectroscopy (MCTS) in which both majority and minority carriers are electrically injected into the probing region. However, it has been reported that  $V_2$  (−/0) can be observed in p-type samples using DLTS in which selective injection of minority carriers is done optically during the filling sequence (this is sometimes called ODLTS) [5]. In turn, in n-type material the acceptor states of  $V_2$ , singly and doubly negative, have been well studied by using DLTS while  $V_2$  (+/0) is not observed by MCTS and ODLTS due to its large electron capture cross section [6].

The  $V_2$  centre is stable up to about 200 °C where it starts to migrate and can be trapped by other defects or impurities. One of the most prominent and abundant traps for  $V_2$  is interstitial oxygen atoms ( $O_i$ ). The annealing kinetics for the acceptor states of  $V_2$  during heat treatment in the 200–300 °C temperature range has been studied in detail for n-type material [7–10]. A gradual shift in the position of the  $V_2$  (= / −) and  $V_2$  (− / 0) peaks takes place due to the loss of  $V_2$

and concurrent formation of two new levels with positions at  $E_c - 0.24$  eV and  $E_c - 0.46$  eV [8]. The transformation occurs with an almost one-to-one proportionality, and the new levels have been assigned to doubly negative and singly negative states of the divacancy–oxygen ( $V_2O$ ) centre [9, 10]. Further, it has also been shown that the rate of formation of the new defect levels is proportional to the oxygen concentration in the samples [10].

In annealed p-type material, a shift in the position of the  $V_2$  (+/0) level to  $\sim E_v + 0.24$  eV has been observed by Trauwaert *et al* [11] using both Czochralski (Cz) and float zone samples. The shift occurs faster in the Cz-samples and it was proposed that the new level is related to  $V_2O$  (+/0) [11]. However, the kinetics of this shift or the intermediate stages of the  $V_2$  to  $V_2O$  transition have not been reported. Recently, Markevich *et al* [12] observed a similar shift of the  $V_2$  (+/0) peak, and it was discussed that the emerging level may be a combination of  $V_2O$  (+/0) and the trivacancy–oxygen centre,  $V_3O$  (+/0). The kinetics of the transformation of  $V_2$  (+/0) was, however, not studied quantitatively and moreover, data on simultaneous formation of the acceptor and donor states of  $V_2O$ , using the same sample, are not found in the literature.

Markevich *et al* [12] discussed, in addition to  $V_2O$  (+/0) and  $V_3O$  (+/0), double-donor states of  $V_2O$  and  $V_3O$ :  $V_2O$  (2+/+) and  $V_3O$  (2+/+). The existence of  $V_2O$  (2+/+) would have a considerable impact on our fundamental understanding of the  $V_2$  and  $V_2O$  centres, which do indeed have very similar atomic structure and electronic properties, as illustrated by their close energy level positions. The existence of  $V_2O$  (2+/+) would throw doubt on the commonly accepted assumption, supported by theory [13], that  $V_2$  (2+/+) is not thermodynamically stable. Moreover, results obtained by Coutinho *et al* [14] predict no  $V_2O$  (2+/+) level in the band gap using the local spin density functional supercell code AIMPRO.

In the present work, we have performed a quantitative DLTS analysis of the transformation from  $V_2$  to  $V_2O$  in proton-irradiated boron-doped p-type Cz-silicon. Employing DLTS and ODLTS, a simultaneous transition for the  $V_2$  (−/0) and  $V_2$  (+/0) states to the corresponding states of  $V_2O$  has been revealed using the same samples, confirming the identification of the  $E_v + 0.23$  eV level as  $V_2O$  (+/0). However, no evidence is found of a double-donor state of  $V_2O$ , but rather the presence of competing traps for migrating  $V_2$  centres.

## 2. Experimental details

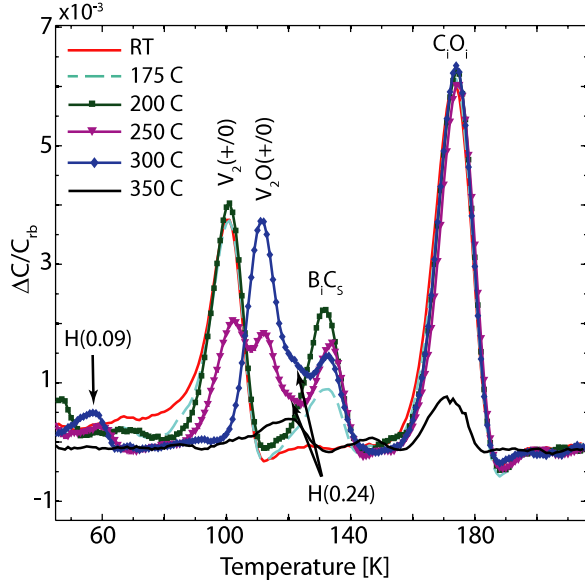
The samples studied were  $n^+p$  diodes fabricated using Cz-silicon wafers with a boron doping concentration of about  $2.2 \times 10^{15} \text{ cm}^{-3}$ . First, the wafers were dry oxidized at 1100 °C for 3 h to grow a 250 nm thick  $\text{SiO}_2$  layer. Standard positive photolithography and wet etching using buffered oxide etch (BOE) were then applied to open holes with a diameter of 200–2000  $\mu\text{m}$  in selected areas. The  $n^+$  layer was formed by in-diffusion of phosphorus (P) from gas phase in a quartz tube. Aluminium (Al) Ohmic contacts were prepared by thermal evaporation on the front (the  $n^+$  side)

and silver paste was used as the contact on the back after removal of the  $\text{SiO}_2$  layers by BOE. The oxygen [O] and carbon [C] concentration in the samples were  $\sim 7 \times 10^{17}$  and  $\leq 2 \times 10^{16} \text{ cm}^{-3}$ , respectively, as determined by secondary-ion mass spectrometry (SIMS). Irradiation of the diodes was performed at RT with 1.8 MeV protons to a dose of  $2 \times 10^{12} \text{ cm}^{-2}$ ; the projected range of the protons was  $\sim 40 \mu\text{m}$ , as estimated by simulations using the TRIM code [15], and far beyond the extension of the region probed in the DLTS (ODLTS) measurements ( $\sim 1 \mu\text{m}$ ). Isochronal annealing (30 min duration) was carried out in air for temperatures in the range of 175–350 °C. During the annealing, out-diffusion of H from the region around the projected range may be anticipated, but no indications of any H-related levels in the DLTS/ODLTS spectra were found. The DLTS and MCTS measurements were carried out by employing a refined version of the set-up described in [16] with forward biases of 0 and 3 V during the filling pulse, respectively. The reverse bias quiescent voltage was kept at 10 V and the temperature was scanned between 40 and 300 K. ODLTS was employed with a filling pulse width of 200 ms using a light emitting diode, having a wavelength of 940 nm and power of 4 mW, for the optical excitation. The illumination was done from the back of the samples and a reverse bias of 10 V was used. A high resolution weighting function (GS4) [17] was applied for the extraction of DLTS and MCTS spectra and a lock-in weighting function for the ODLTS spectra. The activation enthalpies of the transitions are deduced from the emission rates of the charge carriers measured at different temperatures, and the accuracy is around  $\pm 0.01$  eV.

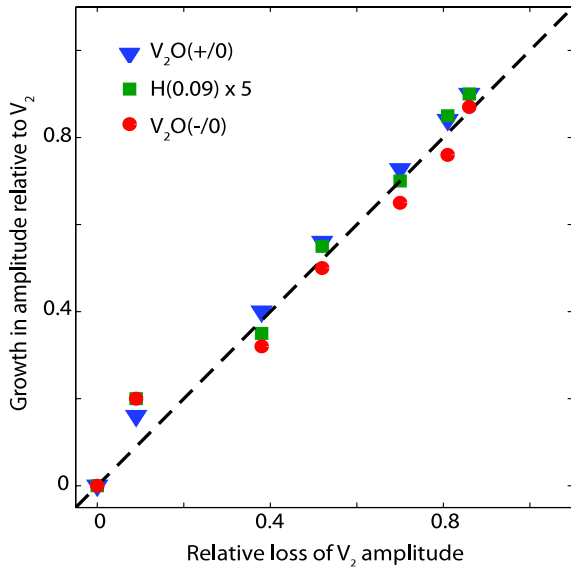
## 3. Results and discussion

Figure 1 shows typical DLTS spectra after irradiation and subsequent heat treatments. The most common defects in the as-irradiated sample are  $V_2$  (+/0) and  $C_iO_i$  [18] with energy levels at  $E_v + 0.19$  eV and  $E_v + 0.36$  eV, respectively. A new level at  $E_v + 0.29$  eV, attributed to interstitial boron–substitutional carbon ( $B_iC_s$ ), appears after annealing at 175 °C [19]. Its amplitude increases with annealing up to 250 °C, then decreases and disappears at about 350 °C. The  $E_v + 0.36$  eV level, which is the most prominent one, is stable up to 300 °C, before decreasing after heat treatment at 350 °C, which is consistent with earlier reports and the annealing kinetics of  $C_iO_i$  [20].

The  $V_2$  centre remains stable up to 200 °C. After 250 °C, the  $V_2$  (+/0) peak has decreased by  $\sim 50\%$  and a new level at  $\sim E_v + 0.23$  eV with an apparent capture cross section of  $\sim 10^{-15} \text{ cm}^2$  emerges (the peak position at  $\sim 113$  K in figure 1). The increase in the amplitude of the  $E_v + 0.23$  eV level exhibits a close one-to-one correlation with the loss of  $V_2$  (+/0), consistent with an assignment to  $V_2O$  (+/0) [11, 12] since  $O_i$  is the dominant trap for the migrating  $V_2$  centres in Cz-samples [7–10]. A further increase of the amplitude of  $V_2O$  (+/0) takes place at 300 °C, as  $V_2$  (+/0) disappears below the detection limit. The close one-to-one proportionality between the loss of  $V_2$  and growth of  $V_2O$



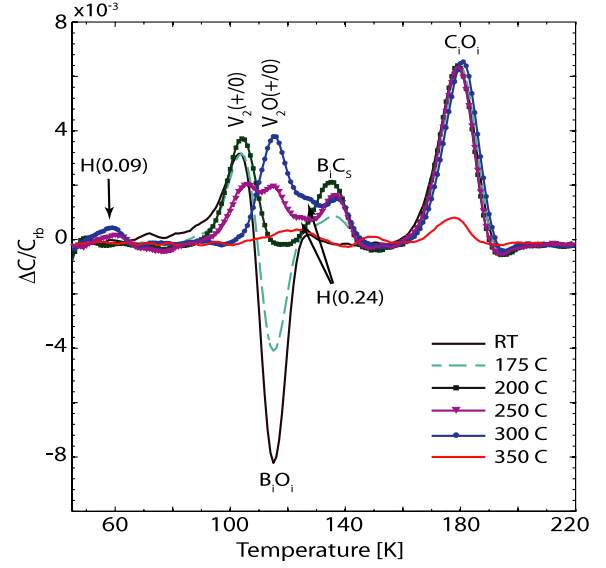
**Figure 1.** DLTS spectra of proton-irradiated and annealed Cz-samples. A rate window of  $(640 \text{ ms})^{-1}$  was used.



**Figure 2.** Growth in  $V_2O$  and  $H(0.09)$  amplitudes, normalized to the initial amplitude of  $V_2$ , versus the relative loss in  $V_2$  amplitude during isothermal annealing at  $250^\circ\text{C}$ . The dotted line represents a one-to-one proportionality between  $V_2O$  growth and  $V_2$  loss.

is also substantiated by the data in figure 2 obtained after isothermal annealing at  $250^\circ\text{C}$ .

After the heat treatment at and above  $250^\circ\text{C}$  a new hole trap arises at  $\sim E_v + 0.09 \text{ eV}$ , labelled  $H(0.09)$  in figure 1. Recently, Markevich *et al* [11] reported a similar level at  $E_v + 0.087 \text{ eV}$  appearing after  $300^\circ\text{C}$  annealing with a one-to-one correlation to the loss of  $V_2$  in epitaxial material, and an identification as  $V_2O(2+/+)$  was suggested. However, figure 1 unveils a concentration of  $H(0.09)$  of only  $\sim 15\%$ – $20\%$  of that of the  $V_2O$  (or  $V_2$ ) level, which excludes the possibility of  $V_2O(2+/+)$  as an origin of  $H(0.09)$ . It should also be pointed out that no other level could be

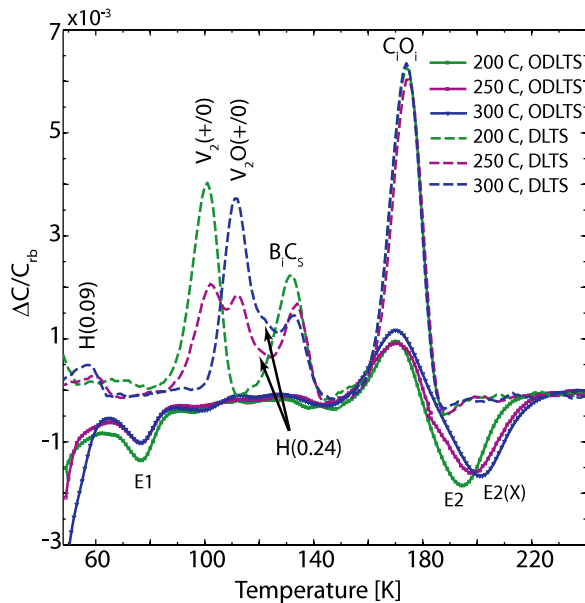


**Figure 3.** MCTS spectra of a proton-irradiated Cz-sample before and after isochronal annealing in the range of  $175$ – $300^\circ\text{C}$  for 30 min. A rate window of  $(640 \text{ ms})^{-1}$  was used.

ascribed to  $V_2O(2+/+)$  in the DLTS spectra. As depicted in figure 1, both  $V_2O(+0)$  and  $H(0.09)$  have their maximum amplitude after the  $300^\circ\text{C}$  anneal and then disappear after  $350^\circ\text{C}$ . In fact, like for  $V_2O$ , the growth of  $H(0.09)$  also displays a close proportionality with the loss of  $V_2$  (figure 2), which indicates that  $H(0.09)$  is due to a centre formed by the trapping of migrating  $V_2$  centres. Assuming a capture radius of the same magnitude as for  $O_i$ , the trap responsible for the formation of  $H(0.09)$ , in the following labelled as X, has a concentration in the range of  $10^{16}$ – $10^{17} \text{ cm}^{-3}$ . This implies a rather high concentration of X and a possible suggestion is the involvement of carbon; cf the SIMS results. Accordingly, because of the competition between  $O_i$  and X, an enhancement of  $H(0.09)$  relative to  $V_2O$  may be expected in oxygen-lean material, such as epitaxial layers [12].

Another defect having a level at about  $E_v + 0.24 \text{ eV}$ , and an apparent hole capture cross section of  $\sim 10^{-15} \text{ cm}^2$ , emerges when the  $V_2(+0)$  to  $V_2O(+0)$  transition takes place; see figure 1. As the level overlaps with those of  $V_2O(+0)$  and  $B_1C_5$ , the defect parameters are deduced by fitting of the DLTS spectra. The concentration of the  $E_v + 0.24 \text{ eV}$  level is  $\sim 30$ – $35\%$  relative to  $V_2$  and a possible identification as  $V_3O(+0)$  has been put forward by Markevich *et al* [11]. In [12], also a level at  $\sim E_v + 0.12 \text{ eV}$ , associated with  $V_3O(2+/+)$ , was reported but no such level is found in the present samples. The  $V_3O$  centre is expected to form via migration and trapping of  $V_3$ , which is a bi-stable defect that can exist in fourfold-coordinated (FFC) and metastable (110) planar configurations. The FFC structure is lowest in energy and has an acceptor level at  $E_c - 0.075 \text{ eV}$  [21], which may be why  $V_3$  is not observed in our as-irradiated samples.

MCTS spectra of the same samples as were used in figure 1 are depicted in figure 3. The MCTS spectrum of the as-irradiated sample is similar to the DLTS one in addition to one electron trap at  $E_c - 0.25 \text{ eV}$ , which is commonly



**Figure 4.** ODLTS and DLTS spectra of a proton-irradiated p-type Cz-sample after annealing at 200, 250 and 300 °C. A rate window of  $(640 \text{ ms})^{-1}$  was used.

identified as an interstitial boron–interstitial oxygen centre ( $\text{B}_i\text{O}_i$ ). However, recent results have shown that the formation and annealing kinetics of the  $E_c - 0.25 \text{ eV}$  level are not fully understood [22]. The amplitude of the  $E_c - 0.25 \text{ eV}$  level starts to decrease after 175 °C and disappears at 200 °C with the growth of  $\text{B}_i\text{C}_s$ , although the latter is a factor of four lower in amplitude. Like DLTS, MCTS also unveils the transition from  $\text{V}_2 (+/0)$  to  $\text{V}_2\text{O} (+/0)$  and the formation of the  $\text{H}(0.24)$  and  $\text{H}(0.09)$  levels. Furthermore, no negative charge state of  $\text{V}_2$  has been detected in the MCTS measurements, indicating large hole capture cross sections of these states [2].

ODLTS and DLTS spectra after annealing are compared in figure 4. The ODLTS analysis reveals two electron traps with positions at  $\sim E_c - 0.17 \text{ eV}$  and  $\sim E_c - 0.44 \text{ eV}$  and identified as the vacancy–oxygen pair (VO) [23] and  $\text{V}_2 (-/0)$ , respectively. A gradual transition of  $\text{V}_2 (-/0)$  to  $\text{V}_2\text{O} (-/0)$  takes place during the annealing, similar to that observed in n-type material [7–10]. Furthermore, within the experimental accuracy, and as illustrated by figure 2, the rate of transition from  $\text{V}_2 (-/0)$  to  $\text{V}_2\text{O} (-/0)$  is identical to that from  $\text{V}_2 (+/0)$  to  $\text{V}_2\text{O} (+/0)$ , firmly establishing the identity of the  $\sim E_v + 0.23 \text{ eV}$  level as  $\text{V}_2\text{O} (+/0)$ . Finally, it should be pointed out that all the levels attributed to  $\text{V}_2\text{O}$ , as well as the VO level, are below the detection limit after annealing at 350 °C (not shown).

#### 4. Conclusions

In summary, a simultaneous transition of the  $\text{V}_2 (-/0)$  and  $\text{V}_2 (+/0)$  states to the corresponding states of  $\text{V}_2\text{O}$  is demonstrated during heat treatment above 200 °C, strongly confirming the assignment of the different levels involved.

The formation of two additional levels at  $\sim E_v + 0.09 \text{ eV}$  and  $\sim E_v + 0.24 \text{ eV}$  occurs during the  $\text{V}_2$  to  $\text{V}_2\text{O}$  transition process. The properties of the latter are consistent with a previous identification as  $\text{V}_3\text{O} (+/0)$ . The former one arises from a complex formed between migrating  $\text{V}_2$  centres and a trap competing with  $\text{O}_i$  and not from a double-donor state of  $\text{V}_2\text{O}$ , as has been suggested in the literature.

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