Evidence for identification of the divacancy-oxygen center in Si

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A deep level transient spectroscopy (DLTS) study of electronic defect levels in 15 MeV electron irradiated *n*-type float-zone Si samples with different oxygen contents has been performed. Heat treatment at 250 °C results in a shift of both the singly negative and doubly negative divacancy (V_2) related DLTS peaks. This is due to annealing of V_2 and the formation of a new double acceptor center. The formation of the new center has a close one-to-one correlation with the annealing of V_2. The annealing rate of V_2 and the formation rate of the new center are close to proportional with the oxygen content in the samples. The new center is identified as a divacancy-oxygen complex.

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Despite the tremendous amount of studies of defects in Si, little is known about electronic properties of multivacancy-oxygen complexes, including the most basic of them—the divacancy-oxygen complex (V_2O). Since oxygen is one of the main impurities in Si, the knowledge of the electronic properties of V_2O is crucial for the understanding of defect interactions in Si. For example, the exact mechanisms for impurity-assisted annealing of the divacancy (V_2) are presently not known but can to a large extent involve the formation of V_2O.

From electron paramagnetic resonance (EPR) studies using heavily electron-irradiated samples it is established that V_2O has at least three different charge states: singly negative, neutral, and singly positive.[1] The exact positions of the electronic levels in the band gap are unknown. Besides, theoretical studies of V_2O predict that it can also have a doubly negative charge state,[2,3] and an experimental observation of V_2O could confirm or disprove this prediction.

Recently, there have been contradicting reports on possible observation of V_2O.[4,5] In Ref. 4, the formation of a center with a midgap level ($E_c-0.545$ eV, where E_c is the conduction band edge) has been observed in high-dose irradiated float-zone (FZ) Si. A correlation between the oxygen content and the formation rate of the center has been found. In samples with less oxygen content, the formation of the center occurs at lower doses, while in samples with higher oxygen content, higher doses are needed in order to form a considerable amount of the centers. This phenomenon has been interpreted in terms of interaction between the radiation-induced monovacancies and oxygen. For low doses, the interaction between the monovacancies and the interstitial oxygen atoms, resulting in the formation of the vacancy-oxygen pair ($V+O_i \rightarrow VO$), dominates. As the dose increases, the concentration of unpaired oxygen atoms decreases and the interaction $V+VO \rightarrow V_2O$ takes place with a higher probability. In the samples with lower oxygen content, the unpaired oxygen becomes exhausted already at a lower dose and the formation of V_2O is enhanced, while in the samples with higher oxygen content, higher doses are needed for the interaction $V+VO \rightarrow V_2O$ to become probable. Later it has been shown that the midgap level has a second-order generation rate as a function of dose.[6] No doubly negative charge state of the defect has been observed in contradiction with the theoretical predictions.

Another possible observation of V_2O has been made in a deep level transient spectroscopy (DLTS) study of the annealing behavior of radiation-induced centers in oxygenated FZ Si.[5] It has been found that heat treatment at 225–300 °C results in a shift of the divacancy (V_2) related peaks, both the singly negative $[V_2(0/-)]$ and doubly negative charge state $[V_2(-/=)]$. This shift is interpreted as annealing of V_2 and the formation of a new center, denoted as *X*, with two charge states: the singly negative $X(0/-)$ ($E_c-0.47$ eV) and the doubly negative $X(-/=)$ ($E_c-0.23$ eV). Capture cross-section measurements in Ref. 5 have supported the identification of *X* as a double acceptor center. Further, because of the fact that the positions of the electronic levels of *X* are close to those of V_2 and the center has two negative charge states as V_2, it is suggested that *X* is electronically and structurally similar to V_2. Moreover, the transition of V_2 to *X* exhibits a close one-to-one proportionality. Based on these considerations and taking into account that oxygen is the main impurity in the samples, it has been proposed that *X* can be tentatively identified as V_2O. This identification is in agreement with the theoretical predictions on the charge states of V_2O.

In this work we have studied the annealing of V_2 and the formation of *X* during isothermal heat treatment using Si samples with different oxygen content. It is found that the annealing of V_2 and the formation of *X* occur at a faster rate in samples with a higher oxygen content. This observation supports strongly an identification of *X* as V_2O.

p^+-n^--n^+ diodes were made using high-resistivity and high purity FZ Si wafers. As a part of the fabrication process, the wafers were oxidized in a dry oxygen atmosphere at 1200 °C for 21 h (samples A and B in Table I) or wet oxidized at 1100 °C for 3.7 h (sample C in Table I).

Subsequently, sample A received a so-called oxygenation treatment, where oxygen was diffused into the wafer from the preformed silicon dioxide layer at the surface. The oxygenation was performed at 1150 °C in nitrogen atmosphere for 80 h. An ordinary silicon diode process with boron and phosphorus implantation and postannealing was then performed and aluminum was used as the metal contact.

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TABLE I. Survey of the samples used in the study.

Sample	Doping, P/cm^3	Oxidation	Oxygenation	Carbon, cm^{-3}	Oxygen, cm^{-3}
A	5×10^{12}	21 h dry at 1200 °C	80 h in N_2 at 1150 °C	$(2-4)\times10^{16}$	$(2-3)\times10^{17}$
B	4×10^{12}	21 h dry at 1200 °C		$\leqslant(1-2)\times10^{16}$	$(1-3)\times10^{17}$
C	3×10^{12}	3.7 h wet at 1100 °C		$\leqslant2\times10^{16}$	$(1-2)\times10^{16}$

Oxygen and carbon concentrations in the samples were measured by secondary ion mass spectrometry (SIMS). The SIMS measurements were conducted utilizing a Cameca IMS 4f microanalyzer using Cs^+ sputtering ions having a net impact energy of 13.5 keV. The Cs^+ ions were rastered over a surface area of $100\times100\ \mu m^2$ and the erosion rate was typically 80 Å/s. Negative secondary ions ($^{12}C^-$ and $^{16}O^-$) were recorded from the central part of the sputtered area (~8 μm in diameter). The crater depth was measured using a KLA-Tencor surface profiler and ion implanted samples were used as standards. The detection limit was $\sim1\times10^{16}$ cm^{-3} for both ^{12}C and ^{16}O. The concentrations of oxygen and carbon in the samples at the depth of the DLTS probing (30–100 μm) are presented in Table I.

The diodes were irradiated at room temperature with 15 MeV electrons and a dose of 4×10^{12} cm^{-2}. Subsequently, the DLTS measurements were performed using a setup described elsewhere.[7] In short, the temperature of the sample was scanned between 77 and 280 K, and the measured capacitance transients were averaged in intervals of a width of 1 K. The DLTS signal was extracted by using a lock-in type of weighting function, and different spectra were obtained with rate windows in the range of $(20\ \text{ms})^{-1}$ to $(2.56\ \text{s})^{-1}$ from a single temperature scan. Concentration, energy level, and capture cross section of the traps were then evaluated from the spectra.

For all the samples DLTS spectra of as-irradiated diodes show the presence of three major peaks with activation enthalpies of 0.43, 0.24, and 0.18 eV and primarily identified as the singly negative divacancy $V_2(0/-)$, the doubly negative divacancy $V_2(-/=)$, and the vacancy-oxygen pair (VO), respectively, in accordance with Ref. 5 and references therein. Similar to the previous observation, the $V_2(0/-)$ peak contains an overlapping contribution from other less stable centers that can be annealed out at and below 200 °C.

Isothermal annealing has been performed for the three kinds of samples (A, B, and C) at 250 °C employing durations between 15 and 3165 min (Fig. 1). All the samples have been annealed simultaneously in one furnace load.

Figure 1(a) shows the results of the heat treatment for sample A. After 15 min at 250 °C the DLTS spectrum demonstrates a close one-to-one ratio between $V_2(0/-)$ and $V_2(-/=)$. This indicates that the $V_2(0/-)$ and $V_2(-/=)$ peaks originate solely from V_2 and do not contain significant overlapping contributions from other centers. After 285 min at 250 °C, a change in position of the $V_2(0/-)$ and $V_2(-/=)$ peaks can be observed. Further annealing for 765 min leads to a considerable (~5 K) shift in the position of both the $V_2(0/-)$ and $V_2(-/=)$ peaks to new positions labeled as $X(0/-)$ and $X(-/=)$. A considerably longer heat treatment for an additional 2400 min (total annealing for 3165 min) leads to a decrease of the peaks amplitude but almost no change in the position. This indicates that the peak positions are stabilized, so that $V_2(0/-)$ and $V_2(-/=)$ are annealed out and only $X(0/-)$ and $X(-/=)$ remain. Figure 2 shows the Arrhenius plot for the observed V_2 and X peaks, where $V_2(-/0)$ and $V_2(=/-)$ are determined from the DLTS spectrum after annealing for 15 min [Fig. 1(a)], while $X(-/0)$ and $X(=/-)$ are taken from the spectrum after annealing for 3165 min.

As can be seen in Fig. 1(b), the annealing behavior of sample B is very similar to that of sample A. After 285 min at 250 °C, one can observe a shift of the $V_2(0/-)$ and $V_2(-/=)$ peaks. The shift increases after the heat treatment for 765 min. The additional annealing for 2400 min (total annealing for 3165 min) results in a decreased amplitude of the $X(0/-)$ and $X(-/=)$ peaks and almost no change in the position.

The results for sample C are shown in Fig. 1(c). The DLTS spectrum after a heat treatment for 15 min at 250 °C shows a close one-to-one ratio between $V_2(0/-)$ and $V_2(-/=)$. However, unlike samples A and B, neither significant loss in the amplitude nor shift in the position of $V_2(0/-)$ and $V_2(-/=)$ are observed after the heat treatments for 285 and 765 min. Only after the extended heat treatment for 3165 min, a shift in the position of both $V_2(0/-)$ and $V_2(-/=)$ can be observed.

At least two minor peaks, appearing at around 160 K, are observed in all the samples (Fig. 1). One can notice that the growth of the peaks occurs in samples A and B after 285 and 765 min, while in sample C only after 3165 min. It is not yet clear whether the coexistence of the growth of these peaks and the transformation of V_2 to X is coincidental or not. However, the amplitudes of the 160 K peaks depend on the material used and it can be speculated that the peaks are oxygen related. Further, a contribution of hydrogen to the formation of the peaks is possible.[8]

The transformation of the V_2 peaks to the X peaks has been quantitatively studied by fitting the DLTS spectra using the apparent capture cross-section values and activation energies deduced from Fig. 2. The spectra have been fitted by varying only the amplitudes of the V_2 and X signals. This transformation is exemplified in Fig. 3, where the amplitudes

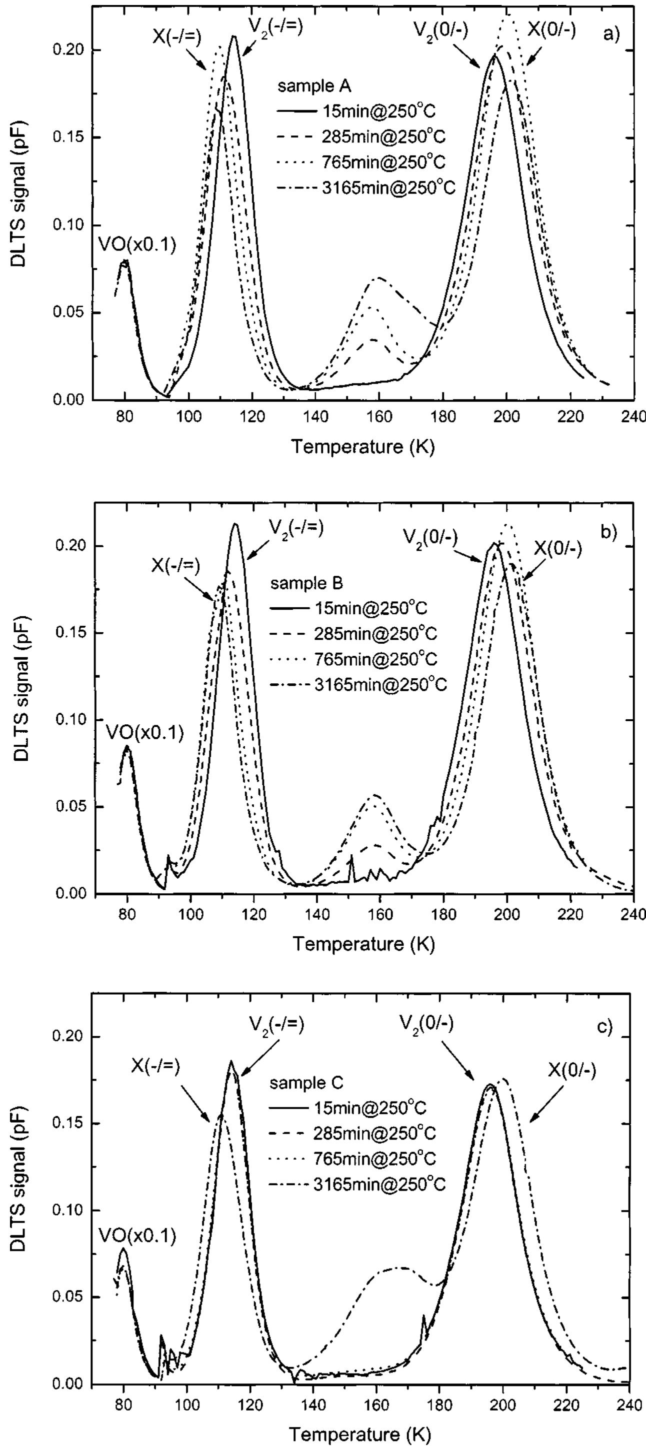

FIG. 1. DLTS spectra for samples A (a), B (b), and C (c) after the heat treatments at 250 °C for different durations. The VO peak in the spectra is multiplied by 0.1.

of the DLTS signals of the $V_2(-/=)$ and $X(-/=)$ peaks are presented as a function of annealing time. It can be seen that the transformation from V_2 to X is considerably slower in sample C. Fitting the amplitudes of $V_2(-/=)$, $X(-/=)$, $V_2(0/-)$, and $X(0/-)$ for samples A, B (not shown in Fig. 3), and C with an exponential decay curve yields the following values of the transformation rate: $(4.6\pm1.0)\times10^{-5}$ s^{-1} for sample A, $(4.3\pm1.0)\times10^{-5}$ s^{-1} for sample B, and $(5\pm1)\times10^{-6}$ s^{-1} for sample C.

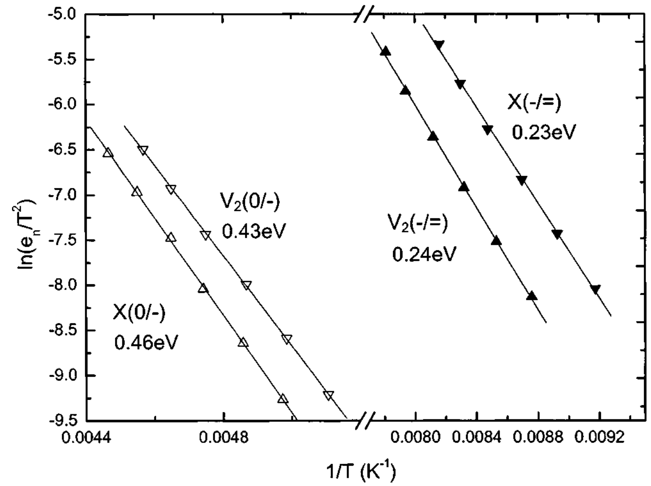

FIG. 2. Arrhenius plot for the $V_2(0/-)$, $X(0/-)$, $V_2(-/=)$, and $X(-/=)$ levels.

The variation in the transformation rates for the samples A, B, and C is in direct correlation and proportional, within the experimental accuracy, to the oxygen content (Table I). This observation supports strongly the previous tentative identification of X as V_2O which is formed through the interaction of migrating V_2 with interstitial oxygen:

$$V_2+O_i\rightarrow V_2O. \quad (1)$$

From previous annealing studies of V_2, it has been concluded that the annealing occurs via interaction with an impurity where V_2's are the migrating species.[8] Since oxygen is the main impurity in Czochralski (CZ) Si, one can expect that the reaction in Eq. (1) should be the dominant mechanism of the impurity assisted annealing of V_2. In reality, no reports on the formation of any double acceptor center dur-

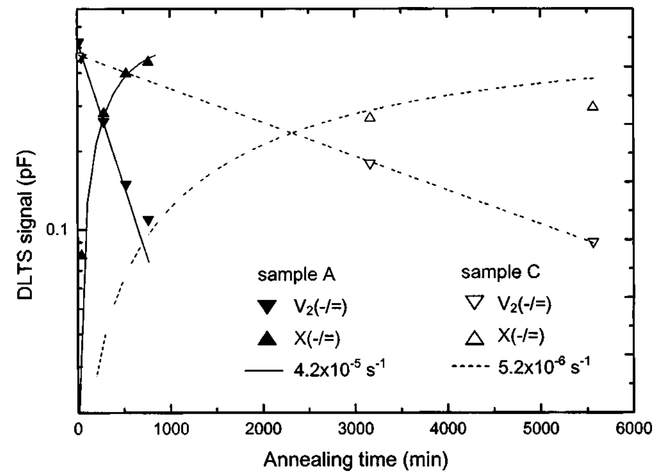

FIG. 3. Amplitudes of the DLTS signals of the $V_2(-/=)$ and $X(-/=)$ peaks as a function of annealing time for samples A and C. The solid and dashed curves represent the exponential decay curves with decay rates of 4.2×10^{-5} and 5.2×10^{-6} s^{-1} for samples A and C, respectively.

ing annealing of V_2 has been presented until recently in either CZ Si or in nonoxygenated FZ Si. Recent results by Markevich *et al.*[9] show the transformation of V_2 to *X* during annealing of electron-irradiated CZ samples with low carbon and hydrogen content, similar to that found in the oxygenated FZ samples.

At least two possible explanations for the absence of earlier reports on the formation of *X* can be put forward. First, the annealing of V_2 occurs via interaction with an impurity that migrates faster than V_2 and has a concentration at least one order of magnitude higher than V_2. In this case, the interaction of V_2 with the fast diffusing impurity can have a higher rate than the interaction with oxygen. Second, the interaction in Eq. (1) has an energy barrier that suppresses the formation of V_2O and it is only surmounted with a sufficient rate at high enough temperatures and/or in the absence of more efficient traps for the migrating V_2's. According to the theory for reaction rates in solids by Waite,[10] it can be calculated that if the energy barrier for the reaction in Eq. (1) exceeds the migration energy of V_2 by ~0.3 eV, the reaction rate is decreased by three orders of magnitude at 200 °C in comparison to that without any barrier.

Finally, the midgap defect observed by Pintilie *et al.*[4,6] has electronic properties different from those of V_2: both in the level position and number of charge states. In contrast, V_2O is established to have a very similar electronic and microscopic structure as V_2.[1] Further, the concentration of the midgap defect is only a small fraction of that of V_2 and the formation rate as a function of dose is of second order. At the present stage, a likely identification of the midgap defect may be the trivacancy (V_3), formed via interaction of vacancies with divacancies: $V+V_2 \rightarrow V_3$. Such an identification can also account for the enhanced formation in oxygen-lean Si and suppression in oxygenated Si. Indeed, in oxygenated Si the migrating vacancies are predominantly trapped by interstitial oxygen, while in oxygen-lean Si more vacancies are available for the reaction $V+V_2 \rightarrow V_3$ and the formation of V_3 is promoted.

In conclusion, we have observed the formation of a double acceptor center during annealing of V_2 in 15 MeV electron irradiated high-purity oxygenated FZ Si samples. Isothermal annealing studies at 250 °C have been performed using samples with different oxygen content. It is demonstrated that the transformation rate of V_2 to the emerging center is directly correlated and even proportional, within the experimental accuracy, to the oxygen content in the samples and a close one-to-one ratio holds for the transformation between the two centers. These observations provide strong evidence that the double acceptor center can be identified as V_2O.

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