Laplace transform transient spectroscopy study of a divacancy-related double acceptor centre in Si

Laplace transform transient spectroscopy study of a divacancy-related double acceptor centre in Si

E V Monakhov[1], G Alfieri[1], B S Avset[2], A Hallén[3] and B G Svensson[1,3]

[1] Department of Physics, Physical Electronics, University of Oslo, PO Box 1048, Blindern,
N-0316 Oslo, Norway
[2] SINTEF Electronics and Cybernetics, PO Box 124, Blindern, N-0314 Oslo, Norway
[3] Solid State Electronics, Royal Institute of Technology, Electrum 229, Kista-Stockholm,
S-16440, Sweden

Abstract
Radiation-induced divacancy-related levels in high-purity oxygen-enriched
n-type silicon have been studied with the use of deep level transient spectroscopy
(DLTS) and Laplace-DLTS. It has been shown that heat treatment at $250\,°C$
results in a shift of the divacancy (V_2)-related peaks observed by 'standard'
DLTS. Using Laplace-DLTS it is demonstrated that the shift is due to annealing
of V_2 and formation of a new acceptor centre. The new centre has presumably
two negative charge states: singly and doubly negative. The formation of
the new centre holds a close one-to-one correlation with the annealing of
V_2, indicating that the new centre is a result of divacancy interaction with
an impurity or a defect. The close position of the electronic levels of the new
centre to that of V_2 suggests a similar electronic and microscopic structure
of the new centre to V_2, and a tentative identification is a divacancy–oxygen
centre.

1. Introduction

Despite the large number of experiments on electrically active centres in Si, little is known
about the electronic properties of multivacancy or multivacancy–impurity centres. Among
these centres, the multivacancy–oxygen complexes are of particular interest. This is due to
the fact that the exact mechanism of impurity-assisted annealing of the divacancy (V_2) in
Czochralski (Cz) and float zone (FZ) Si is not known, and oxygen, as one of the most abundant
impurities in Si, can play a significant role in this mechanism.

One of the first tentative identifications of multivacancy–oxygen centres was made by
Kimerling [1] using deep level transient spectroscopy (DLTS): two of the observed levels with
activation energies of 0.30 and 0.23 eV relative to the conduction band have been assigned to the
divacancy–oxygen (V_2O) and trivacancy–oxygen (V_3O) centres. To the best of our knowledge,
no conclusive evidence for this identification has been reported until now. Later, DLTS studies

of p-type Si suggested transformation of the singly positive charged state of the divacancy [$V_2(0/+)$] into a new centre [2]. It has been proposed that this new centre can be a result of the divacancy–oxygen interaction that forms V_2O. On the other hand, from electron paramagnetic resonance (EPR) studies it is expected that V_2O has at least one negatively charged state (deep acceptor) [3]. Thus, the identification in [2] posed a significant problem since it is known that annealing of V_2 in n-type Si does not result in the formation of a new electrically active centre observed by DLTS [4]. In fact, recent theoretical work has shown that V_2O should have both singly and doubly negative charge states, $V_2O(0/-)$ and $V_2O(-/=)$ [5]. No formation of a centre with two charge states has been observed during V_2 annealing in 'ordinary' n-type Cz or FZ Si.

Recently, we have reported DLTS studies of radiation-induced defects in high-purity low-doped oxygenated Si [6]. It has been found that heat treatment at 225–300 °C results in a shift of the DLTS peaks of both the singly negative $V_2(0/-)$ and doubly negative $V_2(-/=)$ charge states of the divacancy. This shift has been interpreted as a formation of a new double acceptor centre, presumably V_2O, during annealing of V_2.

In order to resolve closely located DLTS peaks, the so-called Laplace-DLTS technique has been suggested [7]. This technique is based on solving the following integral equation:

$$y(t) = \int F(\lambda, t)s(\lambda)\,d\lambda + A + \varepsilon, \tag{1}$$

where $y(t)$ is the measured capacitance transient, $F(\lambda, t)$ is a known function, A is a constant background, ε is an unknown noise component and $s(\lambda)$ is the solution. If one chooses $F(\lambda, t) = \exp(-\lambda t)$, in the case of DLTS and within the Shockley–Read–Hall statistics, the solution $s(\lambda)$ is a sum of delta functions that correspond to emission rates of the deep levels. Thus, the procedure effectively performs an inverse Laplace transform of the capacitance transient, which results in a spectrum of delta-like peaks for a multi- or mono-exponential transient.

In this paper, the Laplace-DLTS technique has been applied in order to resolve the closely located electronic levels and to demonstrate that the shift in the position of the DLTS peaks [6] is indeed due to the formation of a new centre. Moreover, Laplace-DLTS permits determination of the kinetics of V_2 annealing and the simultaneous formation of the new centre, and a close one-to-one relation between the loss of V_2 and the growth of the new centre is revealed.

2. Experimental details

P^+–n^-–n^+ diodes were made using high-resistivity and high-purity FZ-Si. As a part of the processing, the wafers received an oxidation treatment in a dry oxygen atmosphere for 21 h at 1200 °C. Subsequently, a so-called oxygenation treatment was performed in order to increase the oxygen content in the wafers. This was done by diffusing oxygen into the wafers from the silicon dioxide surface layer at 1150 °C in a nitrogen atmosphere for 80 h. Thereafter, an ordinary silicon diode process with boron and phosphorus implantation and post-annealing was performed. Oxygen and carbon concentration in the n^- layer of the diodes, determined by secondary ion mass spectrometry (SIMS), is $\sim 3 \times 10^{17}$ and $\leqslant 5 \times 10^{15}$ cm^{-3}, respectively.

The diodes were irradiated at room temperature by 7 MeV protons with a dose rate of 1×10^9 cm^{-2} s^{-1} and a dose of 8×10^{10} cm^{-2}.

The DLTS measurements were performed using a refined version of the set-up described in detail elsewhere [8]. In short, the sample temperature was scanned between 80 and 280 K and the measured capacitance transients were averaged within intervals of a width of 1 K. The DLTS signal was extracted from the transients applying a lock-in type of weighting function,

and eight traditional DLTS spectra with the rate windows in the range of $(20\,\text{ms})^{-1}$ to $(2.56\,\text{s})^{-1}$ were obtained from a single temperature scan. Concentration, energy level position and capture cross section of the traps were subsequently evaluated from the spectra.

The Laplace-DLTS studies have been performed using a Boonton bridge capacitance meter. The sample is placed in a LN_2 bath-type cryostat equipped with a diode temperature sensor. The use of a diode sensor improves the accuracy of the temperature measurement in comparison with that of a thermocouple since one avoids the uncertainty in the temperature of the second contact of the thermocouple. The capacitance transients are measured repeatedly during about 30 min within a narrow temperature interval, normally ± 0.02–0.05 K, around a pre-set temperature controlled by a LakeShore 330 temperature controller. The transients, which occur within the determined temperature interval, are recorded and averaged. The transients, which either start or end outside the given temperature range, are ignored. The analogous output from the capacitance meter is digitized on-line by a National Instruments data acquisition board E-6011 with a capability of up to 5 million samplings per second and 12-bit resolution. A stored digitized transient consists normally of 5×10^4–5×10^6 points and has a length of 10 ms to 10 s. Before further analysis the transient points are averaged over an interval of 50–5000 points so that the size of a transient is normally reduced to 1000 points. Such an averaging allows a considerable improvement of the signal-to-noise ratio. The averaged transient is then analysed with a general-purpose constrained regularization program CONTIN [9] developed for solving equation (1).

3. Results and discussion

3.1 DLTS measurements

Three dominating peaks associated with the vacancy–oxygen complex (VO), $V_2(-/=)$ and $V_2(0/-)$, can be observed in the DLTS spectra of the as-irradiated diodes. As shown previously, the $V_2(0/-)$ peak has an overlapping contribution from less stable centres that can be annealed out at 200 °C [6]. In order to prepare the samples with pure DLTS signals from V_2, they have been pre-annealed for 2 h at 200 °C. After the pre-annealing, the DLTS spectra demonstrate a close one-to-one ratio between the $V_2(0/-)$ and $V_2(-/=)$ peaks, indicating no significant contribution from other centres (figure 1).

Subsequent isothermal annealing at 250 °C reveals a gradual shift of both the $V_2(0/-)$ and $V_2(-/=)$ peak maxima in the spectra. Heat treatment at 250 °C for 7.5 h leads to a shift of the peak maxima ($\sim$5 K) from the initial position (figure 1). This transformation is interpreted as annealing of V_2 and the formation of a new double acceptor centre denoted as X.

A minor peak appears at $\sim$160 K and gradually grows with the duration of the heat treatment (figure 1). The origin of this peak cannot be readily identified. It can be seen that the growth in the amplitude of this peak does not correspond quantitatively to the change in the amplitudes of the major peaks.

3.2 Laplace-DLTS measurements

The Laplace-DLTS technique has been used in order to demonstrate that the shift of the $V_2(0/-)$ and $V_2(-/=)$ peaks is indeed due to formation of a new centre, as well as to study the kinetics of V_2 annealing and the formation of the new centre. Figure 2 shows Laplace-DLTS spectra, spectral intensity versus the logarithm of emission rate, measured at 119.49 ± 0.02 K after the pre-annealing for 2 h at 200 °C (figure 2(a)) and at 119.68 ± 0.02 K after the heat treatment for 7.5 h at 250 °C (figure 2(b)). In the former case, one observes a dominating peak
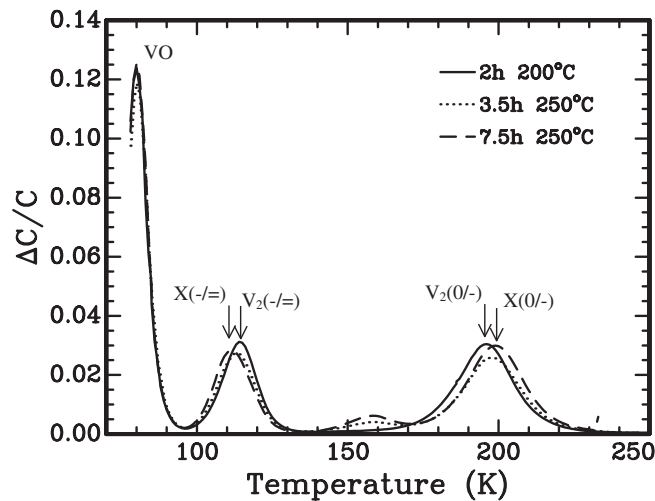
Figure 1. DLTS spectra of the irradiated sample after the heat treatments at 200 and 250 °C.

corresponding to electron emission from $V_2(-/=)$. A smaller peak, labelled $X(-/=)$, can be seen in figure 2(a) at a higher emission rate, indicating the presence of a second centre. The heat treatment for 7.5 h at 250 °C, when a shift of the $V_2(0/-)$ and $V_2(-/=)$ peaks is observed in standard DLTS measurements, results in a reduced intensity of $V_2(-/=)$ and an increased intensity of $X(-/=)$ (figure 2(b)). One can observe that the peaks in figure 2(b) are wider than those in figure 2(a). This can be attributed to somewhat different noise levels and/or thermal fluctuations in the measurements. It should be mentioned that the Laplace-DLTS spectra show the spectral intensity of the emission centres and the amount of the emission centres is given by the integral of a peak. Laplace-DLTS spectra of the $V_2(0/-)$ peak also show the presence of two emission centres denoted as $V_2(0/-)$ and $X(0/-)$. Similarly, $X(0/-)$ grows while $V_2(0/-)$ decreases during the heat treatment at 250 °C.

In Laplace-DLTS measurements it is important to exclude any possibility of misinterpretation of the spectra when, due to the nature of the inverse Laplace transformation, one or several 'false' peaks may appear. Figure 3 presents the Arrhenius plot for the emission rates of $V_2(0/-)$ and $X(0/-)$ (figure 3(a)) and $V_2(-/=)$ and $X(-/=)$ (figure 3(b)) after the pre-annealing at 200 °C and the heat treatments at 250 °C. As can be seen, the electron emission rates of the peaks have an exponential dependence on the reciprocal absolute temperature, and the heat treatment does not change the electron emission parameters of the observed peaks. A small deviation in the emission rates for the $X(0/-)$ peak in the pre-annealed sample can be observed in figure 3(a) (filled circles). This can be explained by large experimental errors which are due to the low intensity of the $X(0/-)$ peak (only ∼10% of $V_2(0/-)$). As the intensity of $X(0/-)$ increases with the heat treatment, the errors reduce and the emission rates are constant with a good accuracy. From the data in figure 3, one can conclude that the $V_2(0/-)$, $X(0/-)$, $V_2(-/=)$ and $X(-/=)$ peaks correspond to real emission centres. The activation enthalpies and the extrapolated electron capture cross sections of the levels are given in table 1.

Figure 4 demonstrates the amplitudes of the peaks as a function of time during isothermal annealing at 250 °C. The amplitudes of $V_2(0/-)$ and $V_2(-/=)$ decrease at similar rates while $X(0/-)$ and $X(-/=)$ increase concurrently. The lines in figure 4 represent the fitting of exponential decay and growth corresponding to first-order kinetics. It can be seen that the growth of both $X(0/-)$ and $X(-/=)$ occurs essentially at an identical rate: the fitting curves
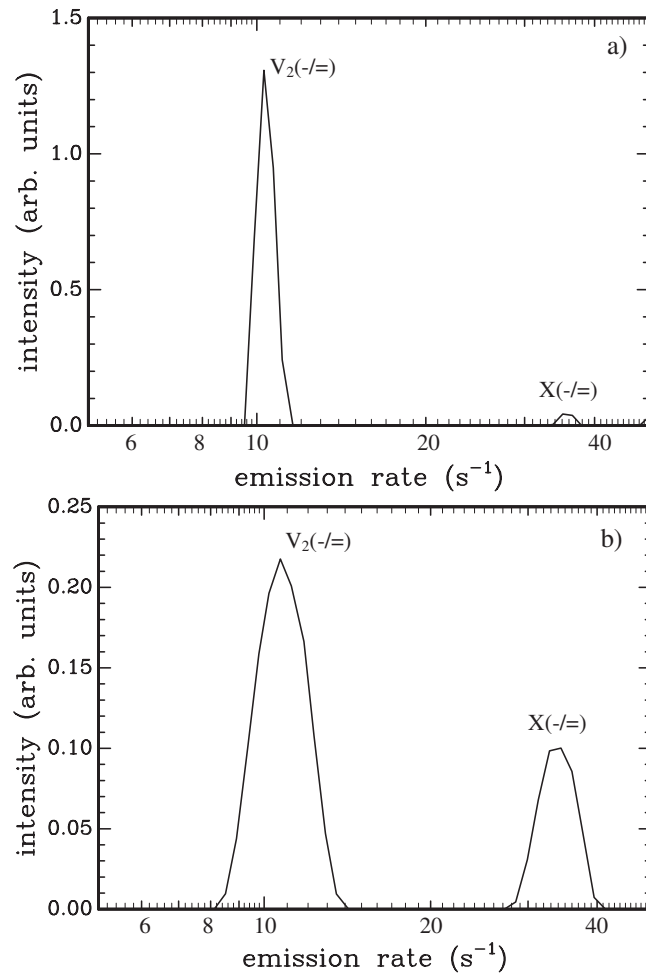
Figure 2. Laplace-DLTS spectra measured at 119.49 ± 0.02 K after the pre-annealing for 2 h at $200\,^{\circ}$C (a) and at 119.68 ± 0.02 K after annealing for 7.5 h at $250\,^{\circ}$C (b).

Table 1. The activation enthalpies and the extrapolated electron capture cross sections of $V_2(0/-)$, $X(0/-)$, $V_2(-/=)$ and $X(-/=)$ deduced from the Laplace-DLTS measurements.

Level	Capture cross section (cm^2)	Activation enthalpy (eV)
$V_2(0/-)$	$(4 \pm 2) \times 10^{-15}$	0.44 ± 0.01
$X(0/-)$	$(3 \pm 1) \times 10^{-14}$	0.49 ± 0.01
$V_2(-/=)$	$(5 \pm 1) \times 10^{-15}$	0.238 ± 0.005
$X(-/=)$	$(6 \pm 2) \times 10^{-15}$	0.231 ± 0.005

for these peaks in figure 4 are practically parallel. This supports strongly the assumption that the peaks labelled $X(0/-)$ and $X(-/=)$ originate from the same centre and represent two different charge states of this centre. The annealing of $V_2(-/=)$ occurs at a rate close to that of the growth of $X(0/-)$ and $X(-/=)$, showing a close one-to-one correlation. Some small but significant deviation in the annealing kinetics of $V_2(0/-)$ from that of $V_2(-/=)$, as well as from the growth kinetics of $X(0/-)$ and $X(-/=)$, is observed. This deviation suggests
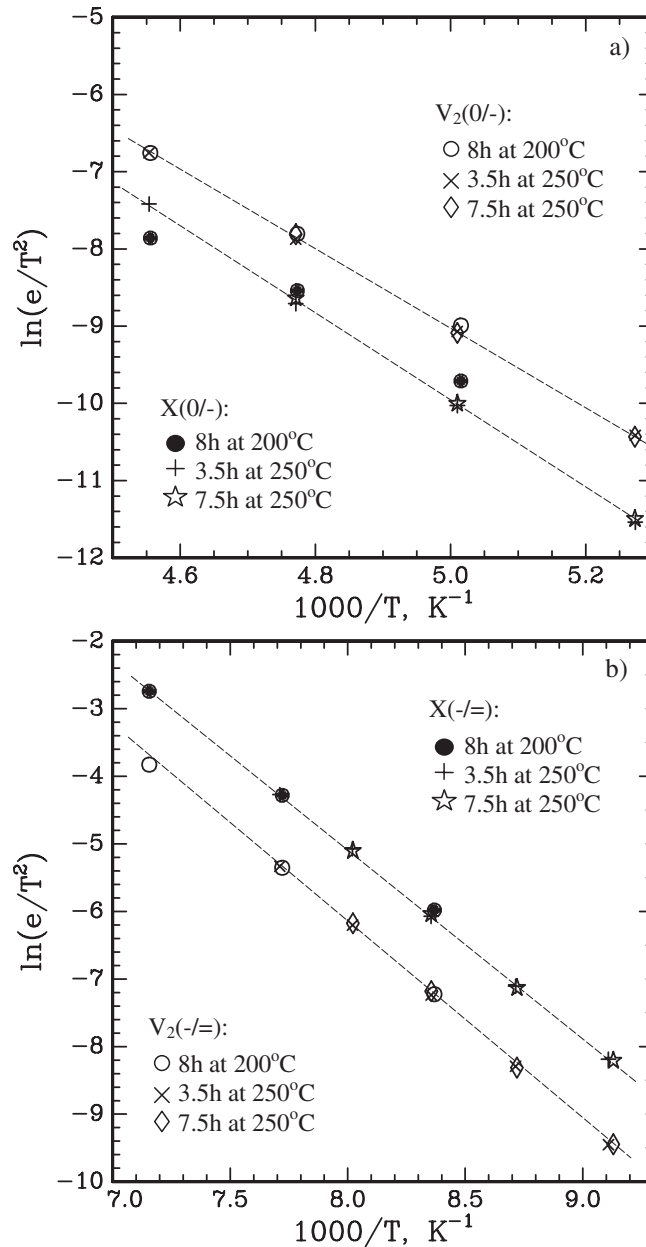
Figure 3. Arrhenius plot for emission rates of $V_2(0/-)$ and $X(0/-)$ (a) and $V_2(-/=)$ and $X(-/=)$ (b) after the heat treatments at 200 and 250 °C. The broken lines are drawn for better presentation of the trends.

the presence of an unresolved peak overlapping with $V_2(0/-)$ and a possible candidate may be a hydrogen-related defect, as has been observed in [10]. These conclusions are further supported by the sums $V_2(-/0) + X(0/-)$ and $V_2(-/=) + X(-/=)$ in figure 4, where the latter stays constant within the experimental accuracy, while the former indicates a small ($\sim$10%) but systematic increase at longer durations.
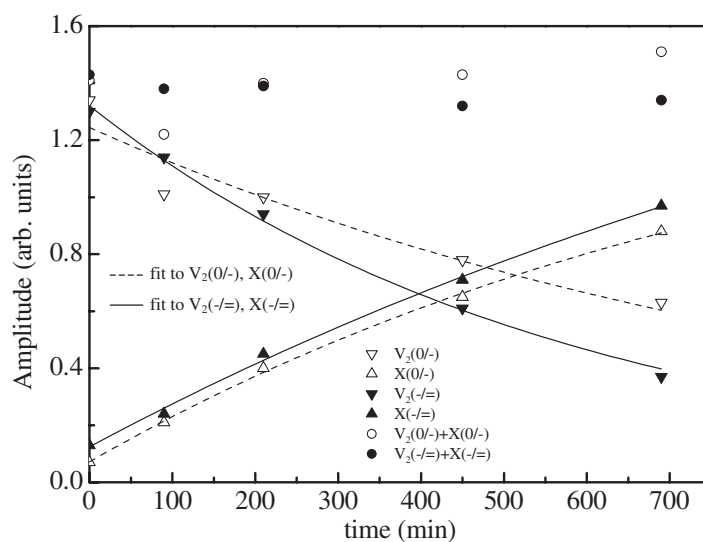
Figure 4. The amplitudes of the peaks as a function of time during isothermal annealing at 250 °C.

4. Conclusions

Radiation-induced divacancy-related levels in high-purity oxygen-enriched silicon have been studied with the use of Laplace-DLTS. It has been shown that heat treatment at 250 °C results in annealing of V_2 and the formation of a new centre, and the transition obeys first-order kinetics. The new centre has presumably two negative charge states: single and double negative. The formation of the new centre holds a close one-to-one correlation with the annealing of V_2, indicating that the new centre is a result of divacancy interaction with an impurity or a defect. The close position of the electronic levels of the new centre to that of V_2 suggests a similar electronic and microscopic structure of the new centre to that of V_2. A possible candidate is the divacancy–oxygen centre.

Acknowledgment

References

[1] Kimerling L C 1977 *Radiation Effects in Semiconductors 1976* ed N B Urli and J W Corbett (Bristol: Institute of Physics Publishing) p 221
[2] Trauwert M-A, Vanhellemont J, Maes H E, Van Bavel A-M and Langouche G 1995 *Appl. Phys. Lett.* **66** 3056
[3] Lee Y-H and Corbett J W 1976 *Phys. Rev.* B **13** 2653
[4] Pellegrino P, Lévêque P, Lalita J, Hallén A, Jagadish C and Svensson B G 2001 *Phys. Rev.* B **64** 195211
[5] Pesola M, von Boehm J, Mattila T and Nieminen R M 1999 *Phys. Rev.* B **60** 11449
[6] Monakhov E V, Avset B S, Hallén A and Svensson B G 2002 *Phys. Rev.* B **65** 233207
[7] Dobaczewski L, Kaczor P, Hawkins I D and Peaker A R 1994 *J. Appl. Phys.* **76** 194
[8] Svensson B G, Rydén K-H and Lewerentz B M S 1989 *J. Appl. Phys.* **66** 1699
[9] Provencher S W 1982 *Comput. Phys. Commun.* **27** 213
[10] Lévêque P, Hallén A, Svensson B G, Wong-Leung J, Jagadish C and Privitera V 2003 *Eur. Phys. J. Appl. Phys.* **23** 5