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Carbon-related radiation damage centres
and processes in p-type Si

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Received 1 September 1989, in final form 6 December 1989, accepted for
publication 27 February 1990

Abstract. This paper is concerned with carbon interstitial (C\textsubscript{i}), \(E_e + 0.28\) eV, and a
carbon-related centre, \(E_e + 0.37\) eV, growing almost simultaneously with the
removal of the C\textsubscript{i} atoms in electron-irradiated p-type Cz-grown Si. An observed
inverse annealing stage of the former defect at \(\sim 275\) K most likely indicates the
existence of internal processes taking place below room temperature which
liberate C\textsubscript{i} as a final product. These processes are in accord with other
experimental findings showing that the concentration of the \(E_e + 0.37\) eV defect is
larger than that of the C\textsubscript{i}. The identity of the two centres found to contribute to the
creation of the \(E_e + 0.37\) eV defect state is discussed.

1. Introduction

The major incorporated impurities in Cz-grown Si during
processing are C and O. Most of the O atoms occupy
bonded interstitial sites (O\textsubscript{i}) binding two host lattice
atoms (Si-O-Si). However, it has been suggested \[1\] that
O could also occupy substitutional sites in the silicon
lattice. Additionally it has been postulated \[2\] that gas-
like oxygen molecules (O\textsubscript{2}) without bonds to silicon
atoms exist in dynamical equilibrium with O\textsubscript{i} and also
that unbound \[3\] interstitial oxygen atoms exist as a
metastable state of the ground state which is the usual
Si-O-Si bridge. The activation energy for migration \[4\]
of the O\textsubscript{i} is \(2.53\) eV, allowing them to become mobile in
the temperature range 400-500 K. Oxygen molecules and
single oxygen atoms are supposed to have a much higher
migration ability than bound interstitial atoms.

C atoms normally occupy substitutional lattice sites
(C\textsubscript{s}). The activation energy for migration \[5\] is \(3.1\) eV.
C\textsubscript{s}, like O\textsubscript{i}, are immobile at room temperature. In the
context of the present work it is important to note that
there is evidence that in some crystals a proportion of the
carbon atoms may be present in an unknown configura-
tion \[6\]. It is well known that Si self-interstitials (Si\textsubscript{i})
produced by irradiation are selectively trapped by C\textsubscript{i}
atoms with which they exchange sites. The created carbon
interstitials (C\textsubscript{i}), \(E_e + 0.28\) eV, have an activation
energy of 0.38 eV \[7\], low enough for them to be mobile at
around room temperature. At temperatures above
\(270\) K C\textsubscript{i} begin to migrate by thermally activated diffusion
\(270\) K C\textsubscript{i} begin to migrate by thermally activated diffusion
to be captured by various traps.

The complexing of the C\textsubscript{i} has been studied intensively
by optical absorption, photoluminescence, EPR, DLTS and
other techniques in recent years. A level around \(0.35\) eV
above the valence band of p-type Si has been correlated
with the C\textsubscript{i}-C\textsubscript{i} pair, the C\textsubscript{i}-O\textsubscript{i} pair and the C-O-V
complex. Recent studies \[8\] have ruled out any correla-
tion of the C\textsubscript{i}-C\textsubscript{i} pair with the \(\sim E_e + 0.35\) eV level. It
has also been demonstrated \[9\] that the \(0.79\) eV C-line
optical transition, the G\textsubscript{15} EPR spectrum attributed to
the C\textsubscript{i}-O\textsubscript{i} pair, and the \(E_e + 0.38\) eV
electrical level observed by DLTS, all originate from the
C\textsubscript{i}-O\textsubscript{i} pair. Given that, a question immediately arises:
what is the identity of the second centre reported by
several authors \[10-13\] as contributing to the creation of
the \(\sim E_e + 0.38\) eV DLTS peak? One of the objectives of the
present work is to try to give an answer to the above
question.

2. Experiment

Moderate energy (1.5 MeV) electrons (dose = \(4 \times 10^{16}\) e\textsuperscript{-}/cm\textsuperscript{2}) were used to introduce deep levels in
boron-doped Cz-grown Si. Irradiations were performed in situ at 80 K. Schottky barrier diodes were fabricated
by aluminium evaporation on pre-polished Si wafers.
C-V measurements gave homogeneous doping concen-
trations of \(\sim 3.5 \times 10^{15}\) B atoms/cm\textsuperscript{3}. C and O concen-
trations have not been measured in the material under
study. However, their values should be of the order of
\(10^{16}\) atoms/cm\textsuperscript{3} and \(10^{18}\) atoms/cm\textsuperscript{3} for C and O respec-
tively, which are typical for a Cz-grown material. The measurements were carried out by using a standard DLTS experimental set-up [14]. Control samples (not having been irradiated) gave DLTS spectra without any feature in the temperature range of 80–350 K.

3. Results and discussion

The broken curve of figure 1 presents the observed spectra after the 80 K irradiation followed by a thermal anneal of the samples at 220 K for 30 min for the purpose of annealing out the vacancies. The two peaks \( \text{H}_1(0.20) \) and \( \text{H}_2(0.28) \) (in this notation \( \text{H} \) stands for holes and the number in brackets denotes the energy depth in eV from the valence band) are associated with \( \text{V}_2 \) and \( \text{C}_i \) respectively. Peak \( \text{H}_2(0.34) \) originates from an oxygen-dependent vacancy-related defect [15] which anneals out in a couple of hours at around room temperature. The disappearance of peak \( \text{H}_2 \) is accompanied by the emergence of the \( \text{H}_2(0.37) \) peak in the spectra (full curve in figure 1). Therefore, it is not unreasonable to consider that the latter defect is carbon-related. However, a careful inspection of the spectra reveals some details which clearly require further elaboration. Firstly, the concentration of the \( \text{H}_2(0.37) \) peak is larger than that of the \( \text{H}_2(0.28) \) peak. This observation becomes more significant when taking into account that some defects \([16,17]\) anneal out below room temperature, the above observations have motivated us to carefully monitor the \( \text{C}_i \) concentration below 300 K.

Isochronal annealing studies performed from \( \sim 160 \text{ K} \) onwards have revealed an increase in the concentration of \( \text{C}_i \) around 275 K (figure 2) just above the temperature where the latter impurities appear to begin migrating. The observed inverse annealing stage certainly reflects a small change in the concentration of the \( \text{C}_i \). Defect concentrations have been calculated from the formula

\[
N = \frac{2 \Delta C}{C_0} (N_A - N_D)
\]

(which is valid since \( N \ll 0.1(N_A - N_D) \)) where \( \Delta C \) is the DLTS amplitude of the peaks, \( C_0 \) the quiescent capacitance of the reverse-biased diodes and \( N_A - N_D \) is the uncompensated acceptor concentration calculated from \( C-V \) plots. The experimental error for each point has been found to be of the order of \( \pm 0.05 \times 10^{14} \text{ cm}^{-3} \) which is smaller than the dimensions of the dots. Noticeably, a repetition of the whole experiment for another sample of the same material gave quite reproducible results.

A facile explanation may be that Si\(_i\) liberated somehow at this temperature could provide the excess \( \text{C}_i \) by removing carbon atoms from substitutional sites. Defects such as divacancy–silicon interstitial complexes [16] or \( \text{O}_i-\text{Si}_i \) pairs [17] have been demonstrated, which could provide \( \text{Si}_i \) by dissociation below room temperature. An inverse annealing stage of the E(0.12) level of the \( \text{C}_i \) in \( n \)-type Si in the temperature range of 125–150 K has been attributed [18] to this mechanism.

The annealing of the \( \text{C}_i \) defect and the parallel formation of the \( \text{H}_4 \) have been studied previously [19] in low-temperature (120 K) electron-irradiated Cz-grown Si. Any inverse annealing stage for the \( \text{C}_i \) has not been reported. However, in \( n \)-type Si, besides \( \text{C}_i \) and \( \text{O}_i \), \( \text{P} \) could also trap \( \text{C}_i \). Particularly, \( \text{C}_i \) has the greatest probability of pairing with the phosphorus [19]. This is not the case for B-doped Si. Thus, \( \text{C}_i \) do not follow the same reaction paths in \( p \)-type and in \( n \)-type Si. Another point is that the selected annealing temperatures in [19] do not allow the detection of the inverse annealing stage—if it exists—in \( n \)-type Si. Remarkably, a larger concentration of \( \text{H}_4 \) in comparison with that of \( \text{C}_i \) cannot be concluded from their results. For the sake of completeness, in figure 2 we also show the evolution of \( \text{H}_2 \) and \( \text{H}_3 \) in the same temperature range. Above \( \sim 290 \text{ K} \) the signal from \( \text{H}_3 \) affected by the emergence of \( \text{H}_4 \). We conclude the presence of \( \text{H}_3 \) by the fact that the peak continues to display charge-state dependent amplitudes, which is characteristic [15] of the \( \text{H}_3 \). Any obvious correlation between the evolution of \( \text{H}_4 \) and \( \text{H}_3 \) and that of \( \text{H}_2 \) cannot be extracted from these results.

It is worth noticing at this point that a number of defects in Si irradiated with low doses show [20] an increase in their intensity prior to destruction for reasons not yet known. It is not a naive assumption that a portion of the \( \text{C}_i \), being initially in a metastable configuration at these low experimental temperatures, convert to

![Figure 1. The broken curve presents the DLTS spectrum of boron-doped Cz-grown Si after irradiation at 80 K and a 30 min anneal at 220 K. The full curve shows the spectrum after a couple of days during which the sample temperature has been cycled in the range of 80–320 K and a final anneal at 320 K for 4 h.](image)
the basic defect configuration prior to the onset of the migration, thus contributing to the increase of the corresponding DLTS signal.

With reference to the above results two more things seem especially noteworthy. Firstly, the above inverse annealing stage has not been observed in similar studies in floating-zone Si, strongly indicating an active role for oxygen in the whole process. Secondly, the emergence of the H₂(0.28) peak in the spectra seems somehow to be delayed (figure 2) with respect to the decay of the H₂(0.28). Although a definite statement about that needs careful and detailed measurements since the emergence of the H₂(0.37) signal is initially masked by the H₃(0.34) peak still present in the spectra, our feeling from these preliminary results is that the H₄(0.37) peak begins to arise at about 290 K. This becomes particularly interesting since similar observations [21] in photoluminescence studies between the C₁ decay and the growth of the C₁-C₂ pair have postulated the existence of precursor defects.

Recent studies [22] have shown that O should be considered the major trap for the C₁ in contrast with previous results [23] which indicated C₂ for that role. Undoubtedly, a significant portion of the C₁ should be trapped to C₂ forming C₁-C₂ not seen in these studies. Taking this into account the excess C₁ liberated during the inverse annealing stage are not sufficient to account for the observed higher concentration of the H₄(0.37) centre in comparison with the H₂(0.28) C₁ peak. A second mechanism, acting in parallel, may be involved in the whole process. Recent optical absorption studies [24] have shown the creation of C₁-O₂ pairs in electron irradiated CZ-grown Si at Tₑ² = 130 K. Since electrical signals from such pairs have not so far been recorded at these low temperatures we could sensibly assume that C₁-O₂ pairs created by the irradiation and locked to electrically inactive configurations convert to active configurations near room temperature, contributing to the further increase of the H₄(0.37) signal.

Comparisons with the results of room-temperature irradiations are not easy since immediately after the irradiation signals from both the C₁ and the carbon-related centre are present in the spectra. This means that the initial C₁ concentration is not known. However, some very interesting remarks could be made. Figure 1 of [25] shows that during successive scans the decrease in the amplitude of the C₁ peak is larger than the corresponding increase of the carbon-related peak. This is not unreasonable if we think [12] that some of the C₁ may go to unknown traps.

Obviously the temperature of irradiation plays an important role in the reaction processes in which the C₁ participates. The temperature at which silicon is subjected to ‘room-temperature’ irradiations affects [26] the sequence of reactions undergone by radiation products. In a recent publication [13] reporting low-temperature irradiations of CZ-grown Si it has been demonstrated that the introduction rate of the carbon-related centres depends strongly upon the experimental conditions. Significantly enough, a peak at Eᵥ + 0.38 eV, which emerged as the C₁ were removed, contains two centres, one of them appearing to grow more than C₁ peak decay by a factor exceeding 2.5. These results are generally consistent with our observations.

A capture cross section analysis employing measurements of the peak amplitude as a function of the filling pulse duration showed that two centres with capture cross sections σ₁ = 5 × 10⁻¹⁸ cm² and σ₂ = 1.2 × 10⁻¹⁶ cm², respectively, contribute in the creation of the H₄(0.37) peak. These measurements also showed that the former centre contributes to about 90% of the H₄(0.37) peak in comparison with the latter centre which is responsible for the remaining 10%.

Although DLTS experiments alone could not suggest a clear identification of a defect, taking advantage of recent results reported in the literature we have come to the conclusion, by all indications so far, that the two aforementioned centres causing the H₄(0.37) DLTS peak are presumably different types of C-O pairs. The arguments which support this suggestion run as follows:

(i) Among the three centres (C₁-O₁, C₁-C₂₁, C-O-V) until recently assumed as possible candidates for the defect, only C₁-O₁ could, without doubt, be considered [9,27] as correct. C₁-C₂₁ has levels at other positions in the gap [8]. On the other hand, the amplitude of the O-V pair peak at Eᵥ - 0.17 eV was not seen to decrease in these studies [20] during the C₁ migration, ruling out the possibility of the creation of the C-O-V defect through the reaction C₁-(V-O) → C-O-V. Creation of the centre through vacancy occupying complexes to C-O pairs either existing [28] prior to irradiation or created through low-temperature irradiation [24] is also excluded on the basis that the H₄(0.37) peak emerges in our spectra near room temperature.

(ii) The two centres have similar activation energies indicating similar chemical structures. However, this is not necessarily true. It is a common finding in the literature that different defect structures may have close energy level positions in the gap.

(iii) The idea that other carbon-related structures may contribute in the H₄(0.37) peak is the least feasible. For example, there is not so far in the literature any definite
association of pairs like C–V or C–B with recognised
electrical activity in the region of \( \sim E_c + 0.37 \text{ eV} \).

(iv) Optical measurements have shown the existence of various types \([5,24,28,29,30-32]\) of C–O pairs in Si, either prior to irradiation or due to the irradiation or after heat treatment of the samples. It is important to note that there are similarities in the structures of C–O related radiation damage centres and the 450–500 °C thermal defects \([33]\).

(v) The various types \([1-3]\) of oxygen incorporation in the Si lattice encourage the assumption of a C\(_i\) pairing with oxygen being in a configuration other than the bonded interstitial. The percentage of the oxygens in that configuration should be small, in agreement with the fact that measurements carried out in oxygen-lean floating-zone Si have shown that the corresponding \( H_{4}(0.37) \) peak arises from one centre only.

4. Conclusions

In summing up, our results support the conclusion that the radiation damage products and processes involving carbon in Si are far from fully understood and are contingent upon experimental conditions. The salient feature of our spectra, that is the essential incongruity between the concentrations of the C\(_i\) and the carbon-related defect, has been considered and interpreted as a manifestation of internal processes in the Si lattice leading to the liberation of C\(_i\). It is hard to figure out all the details of the related processes. The role of oxygen for example seems dominant, though not exactly determined. Finally, we have suggested that the two centres responsible for the \( H_{4}(0.37) \) DLTS peak in Cz-grown Si are basically carbon- and oxygen-related defects (one of them the C\(_i\)-O\(_i\) pair), but with different physical natures, i.e. a different arrangement of their atomic constituents, a fact reflected in the different capture cross sections they have.

Acknowledgments

The author is indebted to the Physics Department of Reading University and especially to Dr P C Banbury for the provision of the research facilities.

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