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

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Abstract. This paper is concerned with carbon interstitial (C_i), $E_v + 0.28$ eV, and a carbon-related centre, $E_v + 0.37$ eV, growing almost simultaneously with the removal of the C_i atoms in electron-irradiated p-type Cz-grown Si. An observed inverse annealing stage of the former defect at ~ 275 K most likely indicates the existence of internal processes taking place below room temperature which liberate C_i as a final product. These processes are in accord with other experimental findings showing that the concentration of the $E_v + 0.37$ eV defect is larger than that of the C_i. The identity of the two centres found to contribute to the creation of the $E_v + 0.37$ 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_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_2) without bonds to silicon atoms exist in dynamical equilibrium with O_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_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_s). The activation energy for migration [5] is 3.1 eV. C_s, like O_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 configuration [6]. It is well known that Si self-interstitials (Si_i) produced by irradiation are selectively trapped by C_s atoms with which they exchange sites. The created carbon interstitials (C_i), $E_v + 0.28$ 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_i begin to migrate by thermally activated diffusion to be captured by various traps.

The complexing of the C_i has been studied intensively by optical absorption, photoluminesence, 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_i–C_s pair, the C_i–O_i pair and the C–O–V complex. Recent studies [8] have ruled out any correlation of the C_i–C_s pair with the $\sim E_v + 0.35$ eV level. It has also been demonstrated [9] that the 0.79 eV C-line optical transition, the G 15 EPR spectrum attributed to the C–O–V complex (K-centre) and the $E_v + 0.38$ eV electrical level observed by DLTS, all originate from the C_i–O_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 $\sim E_v + 0.38$ 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^-/cm^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 concentrations of $\sim 3.5 \times 10^{15}$ B atoms/cm^3. C and O concentrations have not been measured in the material under study. However, their values should be of the order of 10^{16} atoms/cm^3 and 10^{18} atoms/cm^3 for C and O respec-

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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 $H_1(0.20)$ and $H_2(0.28)$ (in this notation H stands for holes and the number in brackets denotes the energy depth in eV from the valence band) are associated with V_2 and C_i respectively. Peak $H_3(0.34)$ 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 H_2 is accompanied by the emergence of the $H_4(0.37)$ 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 $H_4(0.37)$ peak is larger than that of the $H_2(0.28)$ peak. This observation becomes more significant when taking into account that some of the C_i should be trapped by C_s atoms forming C_i–C_s pairs. Unfortunately the states of the latter defect ($E_v + 0.09$ eV, $E_v + 0.05$ eV) [8] are too shallow to be seen by our equipment operating above $T = 80$ K, with rate windows in the range 0.4–2500 s^{-1}.

Attempts to explain the state of affairs depicted in figure 1 inevitably run into difficulties. The question which immediately arises concerns the origin of the additional C atoms which the difference in the concentrations of H_4 and H_2 indicates. The annealing characteristics of the C_i are well known [7,12]. Mindful of the fact that some defects [16,17] anneal out below room temperature, the above observations have motivated us to carefully monitor the C_i concentration below 300 K.

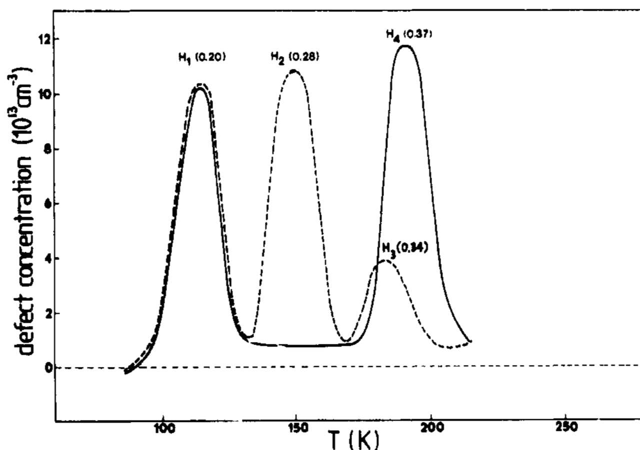

Figure 1. The broken curve presents the DLTS spectrum of boron-doped Cz-grown Si after irradiation at 80 K and a 30 min anneal at 220 K. The full curve shows the spectrum after a couple of days during which the sample temperature has been cycled in the range of 80–320 K and a final anneal at 320 K for 4 h.

Isochronal annealing studies performed from ~160 K onwards have revealed an increase in the concentration of 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 C_i. Defect concentrations have been calculated from the formula

$$N = \frac{2 \triangle C}{C_0} (N_A - N_D)$$

(which is valid since $N \leqslant 0.1(N_A - N_D)$) where $\triangle C$ is the DLTS amplitute 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 $\pm 0.05 \times 10^{14}$ 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 C_i by removing carbon atoms from substitutional sites. Defects such as divacancy–silicon interstitial complexes [16] or O_i–Si_i pairs [17] have been demonstrated, which could provide Si_i by dissociation below room temperature. An inverse annealing stage of the E(0.12) level of the 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 C_i defect and the parallel formation of the H_4 have been studied previously [19] in low-temperature (120 K) electron-irradiated Cz-grown Si. Any inverse annealing stage for the C_i has not been reported. However, in n-type Si, besides C_s and O_i, P_s could also trap C_i. Particularly, C_i has the greatest probability of pairing with the phosphorus [19]. This is not the case for B-doped Si. Thus, 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 H_4 in comparison with that of C_i cannot be concluded from their results. For the sake of completeness, in figure 2 we also show the evolution of H_1 and H_3 in the same temperature range. Above ~290 K the signal from H_3 affected by the emergence of H_4. We conclude the presence of H_3 by the fact that the peak continues to display charge-state dependent amplitudes, which is characteristic [15] of the H_3. Any obvious correlation between the evolution of H_1 and H_3 and that of 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 C_i, being initially in a metastable configuration at these low experimental temperatures, convert to

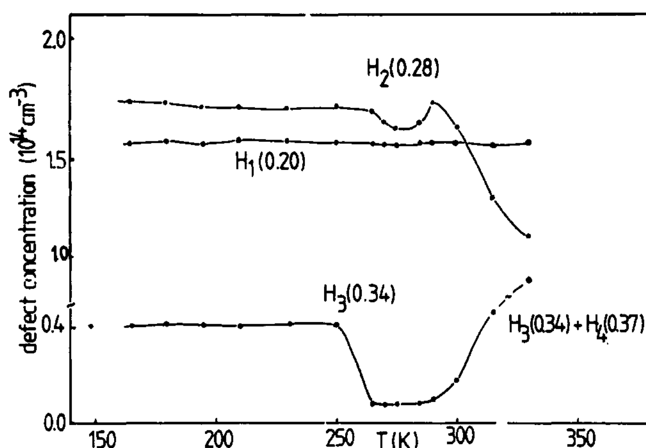

Figure 2. 15 min isochronal anneals of the $H_2(0.28)$ peak of the C_i. The evolution of $H_1(0.20)$ and $H_3(0.34)$ defects is also depicted.

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 $H_4(0.37)$ peak in the spectra seems somehow to be delayed (figure 2) with respect to the decay of the $H_2(0.28)$. Although a definite statement about that needs careful and detailed measurements since the emergence of the $H_4(0.37)$ signal is initially masked by the $H_3(0.34)$ peak still present in the spectra, our feeling from these preliminary results is that the $H_4(0.37)$ peak begins to arise at about 290 K. This becomes particularly interesting since similar observations [21] in photoluminesence studies between the C_i decay and the growth of the C_i–C_s pair have postulated the existence of precursor defects.

Recent studies [22] have shown that O should be considered the major trap for the C_i in contrast with previous results [23] which indicated C_s for that role. Undoubtedly, a significant portion of the C_i should be trapped to C_s forming C_i–C_s not seen in these studies. Taking this into account the excess C_i liberated during the inverse annealing stage are not sufficient to account for the observed higher concentration of the H_4 (0.37) centre in comparison with the $H_2(0.28)$ C_i peak. A second mechanism, acting in parallel, may be involved in the whole process. Recent optical absorption studies [24] have shown the creation of C_i–O_i pairs in electron irradiated Cz-grown Si at $T_{irr} = 130$ K. Since electrical signals from such pairs have not so far been recorded at these low temperatures we could sensibly assume that C_i–O_i 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 $H_4(0.37)$ signal.

Comparisons with the results of room-temperature irradiations are not easy since immediately after the irradiation signals from both the C_i and the carbon-related centre are present in the spectra. This means that the initial C_i 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 C_i peak is larger than the corresponding increase of the carbon-related peak. This is not unreasonable if we think [12] that some of the C_i may go to unknown traps.

Obviously the temperature of irradiation plays an important role in the reaction processes in which C_i 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 $E_v + 0.38$ eV, which emerged as the C_i were removed, contains two centres, one of them appearing to grow more than C_i 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 $\sigma_1 = 5 \times 10^{-18}$ cm^2 and $\sigma_2 = 1.2 \times 10^{-16}$ cm^2, respectively, contribute in the creation of the $H_4(0.37)$ peak. These measurements also showed that the former centre contributes to about 90% of the $H_4(0.37)$ 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 $H_4(0.37)$ DLTS peak are presumably different types of C–O pairs. The arguments which support this suggestion run as follows:

(i) Among the three centres (C_i–O_i, C_i–C_s, C–O–V) until recently assumed as possible candidates for the defect, only C_i–O_i could, without doubt, be considered [9,27] as correct. C_i–C_s has levels at other positions in the gap [8]. On the other hand, the amplitude of the O–V pair peak at $E_c - 0.17$ eV was not seen to decrease in these studies [20] during the C_i migration, ruling out the possibility of the creation of the C–O–V defect through the reaction C_i–(V–O) $\rightarrow$ C–O–V. Creation of the centre through vacancy complexing 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 $H_4(0.37)$ 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 $H_4(0.37)$ 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 $\sim E_v + 0.37$ 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 configuraton 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.

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