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Notes on the Carbon-Associated Deep Level Complex in Irradiated Silicon

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Recent photoluminescence studies on the structure of the two-carbon-atoms pair in irradiated Si provided evidence supporting the hypothesis that the defect comprises a family of related centers with small modifications in their structure. In this communication capacitance transient results are given which point to the same conclusions.

Neuere Photolumineszenzuntersuchungen über die Struktur von Kohlenstoff-Atompaaren in bestrahltem Si haben Hinweise für die Bestätigung der Hypothese geführt, daß die Defekte eine Familie von verwandten Zentren mit geringen Modifikationen ihrer Struktur liefern. Hier werden Kapazitanztransientenergebnisse mitgeteilt, die zu denselben Schlußfolgerungen führen.

1. Introduction

The properties of Si are strongly influenced by the presence of foreign impurities in the crystal lattice. Carbon which is an unintentionally added contaminant in Si is known to form aggregates with various atoms and defects and is probably the impurity most succeptible to complexing. Among these complexes, the two-carbon (or dicarbon) pair, being optically and electrically active, is one of the centers most studied by a variety of experimental techniques. It is always formed in p-Si irradiated at room or liquid nitrogen temperatures when the initially produced carbon interstitials (C_i) migrate around 300 K.

The signature of the defect is: activation energy $E = E_V + 0.33$ eV and capture cross-section $\sigma = 8 \times 10^{-17}$ cm^2 [1]. These parameters were determined by deep-level transient spectroscopy (DLTS) studies [2]. The center has also been associated with the Si-G11 electron paramagnetic resonance (EPR) spectrum [3] initially believed to be a double split carbon interstitial, i.e., a carbon pair sharing a substitutional site. Later EPR studies [4] showed that the two carbon atoms are not equivalent in the pair, one of them being more substitutional-like and the other more interstitial-like. The same defect has been correlated with an optical absorption [5] line at 1.28 μm and a photoluminescence (PL) band [6] at 969 meV. Recent optical detection of magnetic resonance (ODMR) studies [7] have suggested a detailed microscopic model for the center involving two substitutional carbon atoms at adjastent lattice sites separated by an interstitial Si atom which is distorted from the bond-centered position (C_s–Si_i–C_s). However, recently performed theoretical calculations [8] are in agreement with Brower's model [3, 4] considering the center as (111) C_s–C_i pair, which is Jahn-Teller distorted from C_{3v} to C_{1h} symmetry.

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2. Objectives

Recent PL studies [9] have revealed the presence of some other additional lines at 951, 953, and 957 meV exhibiting similar features as those of the 969 meV line. It has also been suggested [10] that the line at 926 meV must be produced by a center similar to the C_s–Si_i–C_s one. These results indicate that the defect forms a family of related complexes with some modifications in their structure, presently of unknown nature. This possibility is not unusual since different modifications of another carbon-related defect, i.e., the C–O pair have also been previously reported [11].

Localized vibrational mode (LVM) spectroscopy studies showed [12] the presence of an unknown defect labelled (C2) appearing between the decay of the C_i defect and the growth of the 969 meV line. It seems that the conversion of the C_i to the di-carbon pair is not a simple process. C_i might transform to another configuration prior to being captured by another C atom leading finally to the C_s–Si_i–C_s structure. The formation of an optically active precursor defect is also possible quickly converting to the defect which produces the 969 meV line. Other centers giving weaker LVM absorptions have been observed as well throughout these stages indicating that clusters of defects must be created [13]. Thus a complete picture of the detailed microscopic identity and the formation mechanism of the center is still lacking.

More significantly, the di-carbon pair has been used recently [14, 15] to determine the carbon concentration in Si beyond the detection limit of usual analytical methods. This important development is restricted to floating-zone (FZ) Si, because in pulled Si, where the oxygen content is higher, the latter element competes with carbon to trap Si_i and O_i atoms.

The primary objective of this work is to focus attention on the subject of the structure of the two-carbon defect in Si. The PL measurements and the DLTS studies lead to the same conclusions. The results indicate that the defect rather consists of a group of related structures.

3. Experimental Results and Discussion

The motivation for this work arose in the study of defects appearing in the DLTS spectrum of boron-doped (ϱ = (6.4 to 7.4) Ω cm) FZ Si Schottky diodes irradiated at 80 K by 1.5 MeV electrons. Fig. 1 depicts the DLTS spectrum after an anneal of the samples at 315 K for 5 h. Each feature in the spectrum is identified by the assigned structure and the number in brackets denotes the energetic position of the corresponding state in the gap. The letter H refers to hole emission rates. For the sake of comple-

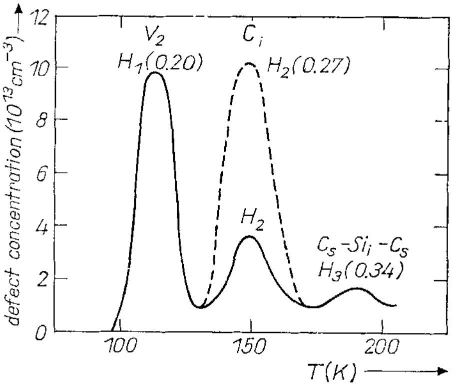

Fig. 1. The solid curve depicts the DLTS spectrum of 1.5 MeV electron-irradiated Si at 80 K after an anneal at 315 K for 5 h. The dashed curve shows the C_i peak immediately after the low-temperature irradiation

teness and also for comparison reasons, the initial amplitude of the C_i peak H_2 (0.27 eV) is shown immediately after the irradiation by the dashed line. Peak H_3 (0.34 eV) is possibly the two-carbon center in FZ Si. This assignment is supported by the following facts:

(i) H_3 should be a carbon-associated center since its growth follows the decay of peak H_2 identified as C_i.

(ii) Although the C and O content has not been measured in our material, it should be around 10^{16} cm^{-3} for both impurities. It has been shown [14] that the capture cross-section for C_s–Si_i–C_s formation is 3.23 times larger than that of the C_i–O_i pair. Thus, the substitutional carbon is the most important trap for the mobile C_i. As regards the C–O–V complex [16, 17] which also gives a level near the same position in the gap we follow similar reasoning. C–O–V is less expected to form in FZ material. According to its formation mechanism [17] the latter complex is produced when a mobile C_i is captured by the O–V pair. Due to the relative low O content in FZ Si, the concentration of the O–V defect is also expected to be low. Hence, the reaction process $C_i + (O\text{–}V) \rightarrow C\text{–}O\text{–}V$ is less efficient than the $C_i + C_s \rightarrow (C_i\text{–}C_s)$ one.

(iii) A capture cross-section analysis involving measurements of the peak amplitude for different pulse durations gave a capture cross-section for H_3 around 1.2×10^{-16} cm^2. This value is in good agreement with previously reported results (1).

The traps depicted in Fig. 1 are already known (1). In this work we have focussed our attention in comparing the concentrations of related defects which has led us to some very interesting conclusions. Providing $N_T < 0.1(N_A - N_D)$, the trap concentration, N_T, was determined by employing the relation

$$N_T = \left(2\,\frac{\Delta C}{C_0}\right)(N_A - N_D)\,, \tag{1}$$

where $N_A - N_D$ is the uncompensated acceptor concentration calculated from C–U plots, ΔC is the experimentally measured capacitance change, and C_0 the quiescent capacitance of the reverse-biased diode. The concentration of the di-carbon center has been found to be around $N_{C\text{-}C} = 1.7 \times 10^{13}$ cm^{-3} (see Fig. 1).

Radiation damage in Si caused by electrons of moderate energy is distributed uniformly in the crystal lattice. The energy that an electron of 1.5 MeV transfers to an atom during collisions is small. Furthermore, the electrons loose energy slowly enough for the damage to be reasonably uniform [18] throughout the samples which are less than half a millimeter thick. Let us suppose that the carbon atoms are distributed randomly, but uniformly, in the Si lattice and there is no correlation between those occupying statistically normal lattice sites in the matrix. A certain fraction of them will be found at adjastent lattice positions. In that case the concentration of these carbon pairs could be determined theoretically [19] by employing the relation

$$N_{C\text{-}C} = \frac{n_m}{2}\,\frac{N_C^2}{N_0}\,, \tag{2}$$

where n_m is the number of nearest neighbors, N_C the carbon concentration, and N_0 the concentration of the lattice sites in Si ($N_0 = 5 \times 10^{22}$ cm^{-3}).

Si crystallizes in the diamond structure. The lattice of diamond is face-centered cubic with two atoms attached to each lattice point. Each substitutional site has four nearest neighbors at a distance of 0.235 nm, 12 next nearest neighbors at a distance of 0.38 nm, etc. [20]. Fig. 2 shows the diamond-type lattice with the four nearest and the twelve second-nearest neighbors to a substitutional site. For $n_m = 4$, 12, or 16 (12 + 4) the calculated carbon content from (2) is found to be around 6.5×10^{17},

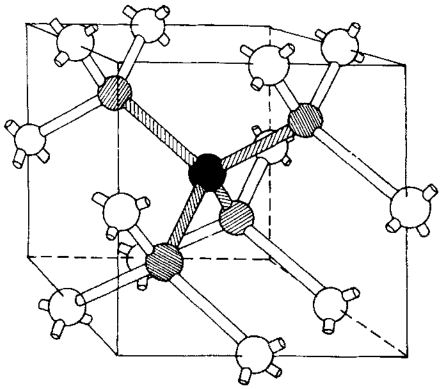

Fig. 2. The first (hatched circles) and the second (open circles) neighbors to a substitutional (full circle) site in the Si lattice

3.8×10^{17}, and 3.25×10^{17} cm^{-3}, respectively. These values are much larger than expected. The solubility limit [13] of C in Si is $(3.6 \pm 0.4) \times 10^{17}$ cm^{-3}. In addition, as indicated in Fig. 1, a considerable amount of C_i has not been converted to di-carbon pairs after 5 h annealing. Consequently, the afore-mentioned values for C in Si are absolutely unrealistic. This fact indicates that either the C atoms are indeed correlated in the host crystal lattice or that the defect under discussion possesses a more extensive nature. In the following, we shall examine these two possibilities separately.

3.1 Carbon atoms are correlated in the Si lattice

In this case (2) is not valid and the carbon content determined by it cannot be compared with the experimental values. However, this correlation between the C atoms should be small [21]. The average distance of the Si lattice sites is roughly equal to $d = (1/N_0)^{1/3} = (1/5 \times 10^{22}\ \text{cm}^{-3})^{1/3} = 2.7 \times 10^{-8}$ cm $= 0.27$ nm. A reasonable carbon content $N_C = 10^{16}$ cm^{-3} in FZ Si gives an average distance between the carbon atoms of about $d_1 = 4.6 \times 10^{-6}$ cm, although for example, for the estimated value $N_C = 3.8 \times 10^{17}$ cm^{-3}, the distance is $d_2 = 1.4 \times 10^{-6}$ cm. The difference between d_1 and d_2 is small. Alternatively, we could say that even if a small fraction of C atoms is correlated, this might be sufficient to account for the estimated higher C concentration by using (2).

3.2 The center has a more extensive nature

This means two things: either the two C atoms of the defect are not in adjacent sites in the Si network or that more than two C atoms are involved in its structure.

In the first case, we can envisage an admixture of different pairs containing various kinds of neighbors. Of course, the electrical level positions of defect pairs are expected to depend, among other factors, upon the distance the constituent impurities are separated. We are bound to accept in this case that all the above postulated pairs produce a group of close-spaced levels in the gap around 0.34 eV above the valence band. Our suggestion does not contradict to the previous experimental findings [9, 10] about the existence of a family of related defects with slight modifications in their structure.

Additionally, it has been found that two EPR spectra [22], Si–G17 and the Si–L7, arise from the two configurations of the E_c–0.16 eV bistable defect attributed to the di-carbon pair in n-Si. In this respect, it is also important to note that recent DLTS studies [23] on electron-irradiated n-Si have tentatively assigned different electrical levels to the C_i–C_s pair and the C_s–Si_i–C_s structure. Evidently, we do not possess the complete picture of the center. However, all these facts open new fields for investigation about the nature and the exact microscopic identity of the defect.

It is also remarkable that the incorporation of a Si self-interstitial in the defect structure, as deduced from ODMR data, has not been confirmed yet by EPR experiments. The presence of Si_i in the center is assumed as reasonable. Since the defect appears preferentially in irradiated Si the incorporation of damage-specific defect constituents, a potential candidate of which is Si_i, is to be expected.

The correctness of the second aspect mentioned above which suggests the involvement of more than two C atoms in the center remains to be seen. Interesting though, it has been reported [24] that oxygen, which is the other major contaminant besides C in Si, may form chain-like structures in the crystal lattice. However, the close energetic positions of the 951, 953, 957, 969, and 926 meV defects spectra, keeping some reservations for the latter line, strongly suggest that these defects share a common basic configuration. In this context, it is reasonable to consider the PL results as indicating modifications, in the structures of the defects and their geometrical arrangements. It is tempting to think about related defects with differences in the positions of their atomic constituents. In any case it is at least premature, based only on the present results, to conclude about additional atomic constituents in the complex structure.

In conclusion, we could say that our results are not at variance with previous experimental findings. Certainly, they stimulate the need for further investigation on the defect. The existence of a correlation between the carbon atoms in the Si lattice does not exclude the possibility of a more extensive nature in the defect under discussion. Nevertheless, the subject of the two-carbon pair in Si is presumably more complicated than previously thought. The chemical nature, the detailed microscopic identity of the defect, and the mechanism governing its formation may hide some interesting points. We believe that a combination of DLTS, PL, and ODMR experiments would provide the final details on the subject.

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