

CHARGE-STATE CONTROLLED BEHAVIOUR OF THE INTERSTITIAL CARBON DEFECT IN CZOCHRALSKI-GROWN Si

C. A. LONDOS

Solid State Section, Physics Department, University of Athens Panepistimiopolis, GR 157 71-Zografos,
Athens, Greece

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Abstract—This communication reports deep-level transient spectroscopy (DLTS) studies of the interstitial carbon (C_i) defect induced in 1.5 MeV electron-irradiated Czochralski-grown silicon at liquid nitrogen temperatures. The amplitudes of the corresponding peak of the $E_c + 0.28$ eV donor state (+1/0) were found to vary after cooling the samples under zero and reverse bias conditions. Among the various interpretations that one could put forward we have finally come to the suggestion of a model postulating configurational bistability for the defect structure with both configurations populated in the neutral charge state.

Keywords: Carbon interstitial, silicon, DLTS, bistable defects.

INTRODUCTION

Silicon grown by the Czochralski (Cz) technique usually contains substitutional carbon atoms in concentrations of the order of 10^{16} atoms cm^{-3} . After irradiation, carbon is finally injected to an interstitial position where, by trapping a Si self-interstitial, it forms a bonded dumbbell structure known as the C-Si interstitialcy with the C and Si atoms located on either sides of a vacancy in the silicon lattice. The carbon interstitial (C_i) is one of the most studied defects in Si. In its positive charge state the centre produces paramagnetic resonance (G12). EPR studies [1] have shown that the defect has a preferential orientation along the $\langle 001 \rangle$ axis in C_{2v} symmetry. In its neutral charge state C_i is detected optically by its electronic transition at 856 meV and by its local lines at 922 and 932 cm^{-1} exhibiting an intensity ratio 2.0:1, a fact that led to the suggestion of a C-Si interstitialcy either with C_{3v} symmetry [2] or with D_{2d} symmetry [3]. The above lines are usually labelled as the C(1) defect. Localized vibrational-mode spectroscopy studies have shown that around room temperature, where the C_i s become mobile, the decay of a C(1) defect is accompanied by the emergence of another band of unknown origin, designated as C(2), prior to the growth of the 969 meV defect attributed to the di-carbon centre. The C(2) defect might possibly be another configuration of the C_i [4]. Recent investigations have also suggested that the C_i defect may exhibit configurational instabilities [5]. It is worth noticing at this point that differences have been found in the lowest energy configuration for different charge states of the C_i in the diamond lattice [6]. Prompted by the above observations, the main purpose of this

communication is to investigate the possibility of the C_i defect exhibiting structural rearrangements.

EXPERIMENTAL

Schottky diodes fabricated from boron-doped ($n \sim 3.5 \times 10^{15} \text{ cm}^{-3}$) Cz-Si were irradiated *in situ* at 80 K by electrons of 1.5 MeV. Measurements for majority and minority traps were carried out by a standard DLTS apparatus such as that described by Lang [7]. The source for the optical excitation of the minority traps was a GaAs laser.

DLTS has proved very useful in studying the alternative structure of defects in semiconductors. The basic procedure [8] to reveal configurational instabilities of a defect involves the application or not of a reverse bias during the cooling of the samples from a high enough temperature to set the defect in the desired charge state. In the case of a bistable defect in each charge state one of the two configurations is usually favoured at low temperatures (that is, temperatures smaller than those where the transformation of the configurations occurs). Thus setting the defect in a particular charge state and cooling down results in establishing the corresponding configuration. Typically each configuration has a characteristic DLTS spectrum. Hence, configurational instabilities, if they exist, are manifested as changes in the corresponding DLTS spectra.

RESULTS AND DISCUSSION

C_i in a *p*-type Si material gives rise to a level $\sim E_c + 0.28$ eV [9]. Figure 1 represents the DLTS

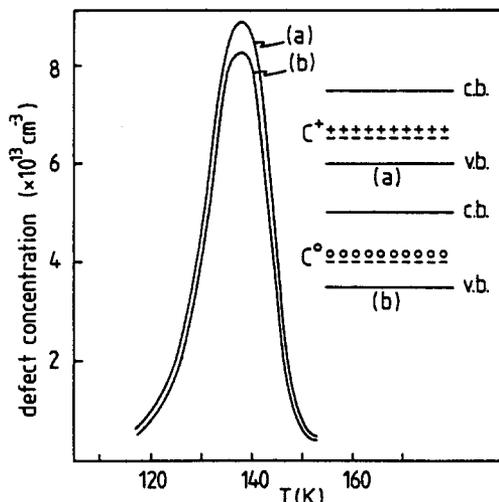


Fig. 1. DLTS spectra of the C_i defect in Cz-Si, boron-doped ($n = 3.5 \times 10^{15} \text{ cm}^{-3}$), showing the result of cooling with (a) zero bias and (b) 5 V reverse bias with annealing temperature 265 K ($\tau_p = 5 \text{ s}^{-1}$).

spectrum of the C_i defect as recorded in our measurements after cooling with bias off (a) and bias on (b) conditions. It is observed that the amplitudes of the corresponding peak are larger when cooling without the application of a bias.

In a first attempt to interpret the results one might consider the above observations as the result of an interaction between the two levels that C_i introduces in the gap. As is well known, C_i is an amphoteric impurity in Si, and besides the donor level (+1/0) at $E_c + 0.28 \text{ eV}$ it also introduces an acceptor (-1/0) at $E_c - 0.12 \text{ eV}$, observed only in n -type Si so far [5]. This level, expected as a minority trap in p -type Si, has never been traced. Our measurements also gave negative results. The introduction of minority carriers (electrons in our case) requires optical illumination. However, under injection conditions majority carriers are also present at densities larger than those of the minority carriers. The time dependence of the electron concentration of a minority trap in a p -type material is given [10] by

$$n(t) = \frac{C_n N}{C_n C_p} (1 - \exp(-C_n + C_p)t).$$

It is clear that the occupancy of a centre in the minority half of the gap and thus its appearance in the spectrum will be determined by the relative values of the corresponding capture rates C_n and C_p for electrons and holes. The very fact that such a trap is missed in our spectra may show that the capture cross-section and generally the capture rate for the electrons are smaller than those for the holes. Notably, the absence of the $E_c - 0.45 \text{ eV}$ level of the interstitial boron from the minority spectrum in p -type silicon has been attributed to similar reasons [11].

In the line of the present argument it is assumed that the two levels of the C_i are more or less effectively coupled together. The application of a reverse bias shifts the Fermi level above the $E_c + 0.28 \text{ eV}$ level which fills up with electrons. In this situation, a partial charge transfer might be promoted towards the $E_c - 0.12 \text{ eV}$ state resulting in a decrease of the measured amplitude of the $E_c + 0.28 \text{ eV}$ level. In other words the application of the reverse bias annealing made feasible a communication between the majority and the minority states within the gap. The relatively large distance between the two levels in the gap is reflected by the low intensity (small amplitude changes) which characterizes the phenomenon. Under zero bias conditions the Fermi level is situated below the $E_c + 0.28 \text{ eV}$ level, which is now empty of electrons, and communication is not possible. If this explanation is correct, thinking the other way around, we may consider the changes in the amplitudes of the $E_c + 0.28 \text{ eV}$ level of the C_i as indirect evidence of the existence of the $E_c - 0.12 \text{ eV}$ level in p -type Si.

In a previous paper [12] we have reported similar behaviour for the C_i peak in float-zone Si. The phenomenon has been interpreted there by considering the ability of the C_i atoms to neutralize some of the vacancies of the B_i-V centre. A similar suggestion could be put forward here as well since the source of vacancies might presumably be the $E_c - 0.34 \text{ eV}$ centre [13].

In the following we shall present an alternative explanation which invokes bistability for the C_i defect, postulating two configurations, A and B, for its structure. When cooling the sample without bias, the defect level lies above the Fermi level, the trap captures holes (Fig. 1), the positive charge state C^+ is attained and thus the favourable configuration, say A, is established. On the other hand, cooling the sample with bias on it shifts the Fermi level above the defect level, the trap becomes empty of holes and thus the neutral charge state C^0 is attained. If the other configuration, say B, is now favourable, then the defect is transformed to it.

At this point, and for the purpose of a better presentation of our interpretation of the phenomenon, we shall elaborate more on the subject of bistable defects. Bistability in general is a situation where a defect exhibits two geometrical configurations, each of which has its own electron levels. In such a case it is usually suitable to consider the energy level scheme of the defect as an explicit function of its spatial configurations. This is schematically illustrated in a diagram depicting the total energy of the defect as a function of a generalized coordinate Q . In one dimension a bistable defect could be pictured by a curve having two energy wells separated by a potential barrier. The stable configuration of the defect will be that of the lower total energy. However, the values of the total energy minima and the height of the separating barrier may change with the charge state. It is then possible for the one configuration to be stable in

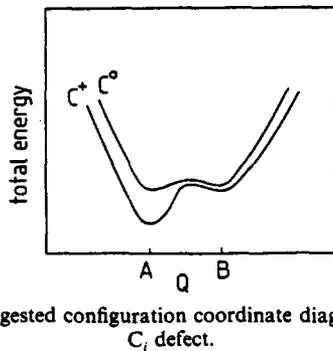


Fig. 2. Suggested configuration coordinate diagram for the C_i defect.

one charge state and the other configuration to be favourable in the other. In this case the order of the relative positions of the two energy minima is inverted between the two charge states. However, it is also possible for the stable configuration to be the same if its energy continues to be minimum in both charge states. The latter case seems to fit with the results for C_i .

Figure 2 depicts the configuration coordinate diagram we have inferred for the C_i defect. In this diagram, configuration A is the stable one in both the positive and the neutral charge states. However, in the neutral state the values of the minima in both configurations take similar values (the total energy continues to be slightly lower in A) and the potential barrier separating them becomes adequately low, allowing A and B to be populated simultaneously. In other words, the change in the charge state from C^+ to C^0 results in a change of the relative position of the energy minima of the two defect configurations modifying the partition of the populations of A and B at the neutral charge state. More specifically, in Fig. 2 the energy of the defect in configuration A, which gives rise to the $E_c - 0.28$ eV peak, increases more in the neutral charge state than in the positive charge state, and approaches the values of the metastable configuration B. The separating barrier becomes adequately low to be surmounted, allowing both configurations to be populated. (Theoretically it is also possible for the energy minimum in B to decrease or both minima in A and B to change, finally attaining close values.) Configuration B is hardly detected by DLTS because most centers being in this configuration are converted to the more stable A before charge transfer at B may be detected. The changes in amplitudes of the peak $E_c - 0.28$ eV show that practically all the defects appear in configuration A. Only a small percentage of them (less than 10%) transform to B during DLTS measurements. However, although the transformation $A \rightarrow B$ could not be driven to completion, the conversion $A \rightleftharpoons B$ is completely reversible.

Unfortunately, the kinetic of the $A \rightarrow B$ and $B \rightarrow A$ transformations were not investigated in the present studies. The annealing behaviour of the defect under zero and 5 V reverse bias is depicted in Fig. 3 for temperatures below the onset of the migration of

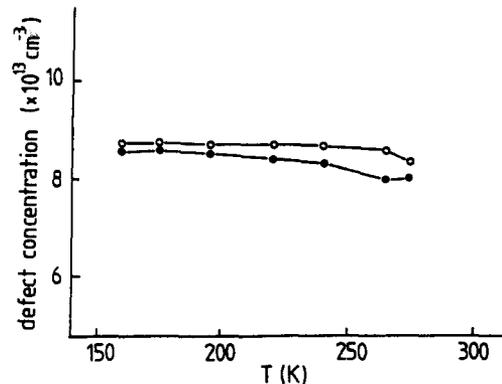


Fig. 3. Five-minute isochronal annealings under zero (O) and under 5 V reverse (●) bias for the C_i defect.

the C_i s. A small tendency for the magnitude of the metastability to increase with the annealing temperature is observed. The fact that the defect remains mostly in configuration A gives reasons for the previous assumption [14] that the atomic structure of the defect is independent of the charge state.

Obviously, a weak point of our model is the fact that no other peak has been detected in the spectra associated with configuration B. We have to assume that in B the defect does not introduce levels in the gap, or that they pass undetected by DLTS. The change in the amplitude of the C_i peak is about the same in all the operating rate windows from 0.4 to 2500 s^{-1} .

Of course, the charge-dependent amplitudes of a defect cannot be considered as a sure indication that it is metastable. As we discussed above, other also physically plausible interpretations could be put forward. Nevertheless, despite the doubts that one could harbour due to the poorness of the data and mainly the lack in the spectra of a peak in configuration B exhibiting complementary behaviour with the $E_c + 0.28$ eV peak in configuration A, we tend to espouse the notion of a bistable defect. At first, the existence of electronic levels in both configurations is not imperative to ensure metastability for a defect. Secondly, bistability is not inconsistent with previous claims that C_i may exhibit configurational instabilities [4, 5]. The completely reversible behaviour in the amplitudes of the C_i peak between the two charge states is also another corroborating point. It should not escape our attention also that defects of an interstitial nature show a trend to display more than one lattice configuration [15]. This is physically understood since interstitial defects in semiconductors could occur in both covalently bonded (for example split, bond-centred) and non-bonded (for example tetrahedral, hexagonal) configurations [16]. Finally, it should be noticed that it has been recently concluded [17] by virtue of optical and electrical results that C_i shows bistability, with the same configuration being the stable one in both charge states.

Developing our model further, it may be suggested that in the positive charge state the defect is in

C_{2v} symmetry as inferred by EPR investigations. However, in the neutral charge state we may speculate that a fraction of the carbon interstitials enter another symmetry, presumably D_{2d} . The latter symmetry is compatible with distortion to C_{2v} , and also consistent with IR observations [3]. In D_{2d} symmetry the C_i atoms may transfer to an electrically inactive state.

CONCLUSIONS

In conclusion, we have presented an explanation to account for the charge-state controlled behaviour of the C_i peak in the DLTS spectra. All of them are speculative, but have some rationale, and cannot be ruled out in the present stage of knowledge about the defect. However, the weight of evidence points towards the assumption of a bistable defect, a fact not inconsistent with the results of other experimental techniques.

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