PHYSICAL REVIEW B VOLUME 35, NUMBER 12 15 APRIL 1987-II

Deep-level transient spectroscopy studies of the interstitial carbon defect in silicon

C. A. Londos
Department of Physics, Solid State Section, University of Athens, 104, Solonos Street, 106 80 Athens, Greece

(Received 29 September 1986)

We report deep-level transient spectroscopy studies of the carbon interstitial (C_i) defect created in boron-doped silicon after electron irradiation at 80 K. The peak amplitudes of C_i have been seen to vary in the spectrum under different bias annealing conditions. The phenomenon is tentatively attributed to the tendency of the C_i defect to annihilate the vacancy of the boron substitutional—vacancy (B-V) pair. This tendency is particularly favored by the charge states of the present defects when cooling the sample with applied reverse bias.

INTRODUCTION

The carbon interstitial defect in silicon has already been studied in detail. The results of variety of experimental methods have contributed to a well-established picture. From EPR measurements[1] for example we know that carbon, a natural impurity in silicon originally at a substitutional site in the lattice, forms a $\langle 100 \rangle$ interstitial defect by trapping a mobile silicon interstitial (Si_i) atom created as a primary defect after the electron irradiation. Infrared spectra show two bands at 922 and 932 cm^{-1} which are identified with a single interstitial carbon atom.[2]

Deep-level transient spectroscopy (DLTS) studies have shown[3,4] that in n-type silicon, C_i introduces two charged energy states in the gap, an acceptor state around $E_c - 0.10$ eV acting as a majority-carrier trap and a donor state around $E_v + 0.28$ eV acting after injection as a minority-carrier trap. In p-type silicon the $E_v + 0.28$-eV level appears always as a majority-carrier signal.[5,6] Nobody, to the best of our knowledge, has ever reported the observation of the $E_c - 0.10$-eV level, expected as a minority-carrier trap in p-type silicon. However, the identification of the latter level in n-type silicon as the C_i defect has been seriously questioned recently.[7] In a comprehensive and detailed report it has been argued that this level should be assigned to a vacancy-related defect.

In this work we present results which show the influence of a charge-state effect in the peak amplitudes of the $E_v + 0.28$-eV level of the C_i defect. We have correlated this behavior with the ability of C_i to annihilate the vacancy of the B-V pair.

EXPERIMENTAL

Schottky diodes were fabricated from boron-doped float-zone-grown (0.85—1.15)-Ω cm and pulled (3—5)-Ω cm silicon material. The sample preparation procedure and the DLTS equipment used have been reported elsewhere.[8] The available rate windows were operated in the region of 0.4—2.500 s^{-1}. The minority-carrier trap spectrum (MCTS) was studied by using a GaAs laser as a source of optical excitation. It provided pulse widths up to 60 msec which were long enough to fill a trap and reach steady-state conditions. Defects were produced by *in situ* irradiation at 80 K with 1.5-MeV electrons from a Van der Graaf accelerator, to a total dose of $\sim 10^{16}$ electrons/cm^2 and a beam current of $\sim 0.1\ \mu A/cm^2$.

RESULTS AND DISCUSSION

The main features of the majority-carrier spectrum of p-type silicon after liquid-nitrogen-temperature electron bombardment have been reported recently.[9] Immediately after the irradiation, C_i ($E_v + 0.28$ eV) appears as one of the dominant levels in the DLTS spectrum. It has been detected both in our float-zone-grown and pulled silicon material. MCTS measurements have shown no evidence of the $E_c - 0.10$-eV level. This fact does not exclude the possibility that the level may remain undetected since certain conditions must be met for the production of a minority-carrier capture transient.[10,11]

After that, our interest was concentrated on the $E_v - 0.28$-eV level of C_i. Five-min isochronal annealings were performed under different bias conditions and the peak heights of this level were carefully monitored. A clear variation in the amplitudes of the C_i level was observed between different annealings under zero and under 5-V reverse-bias conditions. The annealings were always followed by a quenching of the samples at 80 K prior to beginning the DLTS measurement. The concentration was always larger after the zero-bias annealing. The phenomenon is displayed in Fig. 1. For the slowest available rate window of 0.4 s^{-1} the observed differences in the amplitudes were up to $\sim 15\%$ for different annealing temperatures for the float-zone-grown and significantly less for the pulled material. This point will be discussed later.

Curves (a) and (b) in Fig. 2 have been obtained in two different ways. In the first way the experimental data were taken as follows: The sample was annealed at a certain temperature under zero bias for 5 min and then quenched to 80 K and then the DLTS began pulsing. The defect concentration of the obtained peak specifies the experimental point for curve (a) for that annealing temperature. A 5-V reverse-bias annealing at the same temperature gave the corresponding point for curve (b). The next pair of points was taken after subsequent annealings under zero and 5-V reverse bias at a higher temperature and so forth. In the second set of experiments the experimental

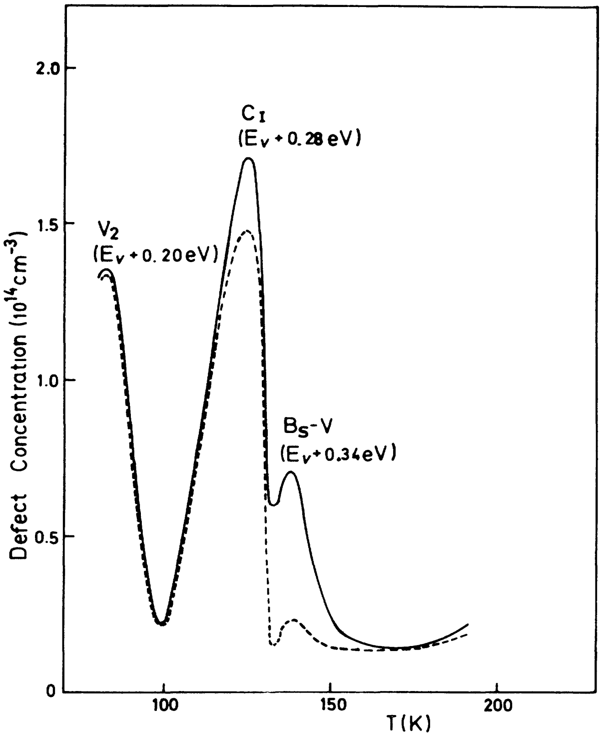

FIG. 1. Typical DLTS spectrum of float-zone p-type silicon following 1.5-MeV electron irradiation at 80 K (rate window 0.4 s^{-1}). The displayed curves has been obtained after 5-min annealings, at $T=215$ K, under zero-bias (solid curve) and 5-V reverse-bias (dashed curve) conditions and quench to 80 K prior to beginning the DLTS measurement.

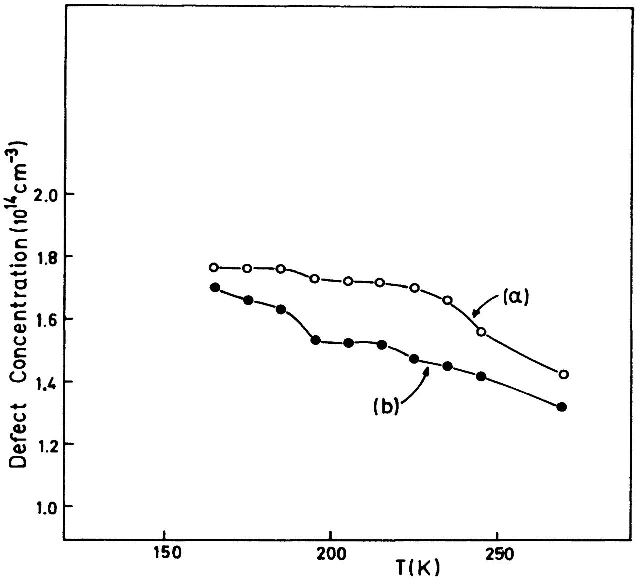

FIG. 2. (a) 5-min isochronal annealings under zero bias of the Ev+0.28-eV level of the C_i. (b) The same procedure under 5-V reverse-bias conditions.

data of curve (a) were taken after annealing at different temperatures under zero bias. Annealings under reverse bias at different temperatures gave curve (b). No significant differences were observed between the corresponding curves obtained with the two experimental procedures.

It is difficult to visualize a model to explain in detail the above behavior. We may think of a charge-state dependence of the ability of the carbon atom to capture the silicon interstitial atom. Under zero-bias annealing this ability is greater, resulting in a stronger signal in the spectrum. Consistent with this assumption is the existence of a trap which competes with carbon in capturing the silicon interstitial and which is more effective under reverse-bias conditions resulting in a lower amplitude of the C_i signal. However, such a trap has not been detected in our transient capacitance measurements. This fact does not exclude its existence. There are two possibilities. At first, the trapping of the Si_i by an unknown atom may lead to an electrically inactive complex. A possible candidate is the oxygen interstitial (O_i) atom which forms the Si_i-O_i complex. However, there is experimental evidence suggesting that the O_i atoms are unimportant as traps for Si_i at least in boron-doped silicon.[12] Another possibility becomes evident through the reaction $Si_i+B \rightarrow B_i$. The boron concentration in our float-zone-grown specimens is $\sim 1.7\times10^{16}$ cm^{-3} which is not low compared with the irradiation doses. This means that the reactions $Si_i+B\rightarrow B_i$ may not be complete and so there is room for competition between boron and carbon in capturing silicon interstitials. In our pulled specimens where the boron concentration is an order of magnitude lower (3.7×10^{15} cm^{-3}) the strength of the phenomenon is smaller. Considering this second assumption to be true, an experimental verification will be difficult since in p-type silicon the $E_c-0.45$-eV level of the B_i proceeds undetected in the minority spectrum.[13]

The fact that no complementary behavior has been observed between the $E_v+0.28$-eV level and any other level in the spectrum cannot rule out the possibility of a metastable defect. It may be argued that when monitoring the $E_v+0.28$-eV peak after cooling the sample with applied reverse bias, part of it has been transformed to another configuration giving rise to a signal which either proceeds undetected by DLTS (Ref. 14) or produces a peak below 80 K and thus beyond the limits of our equipment. According to this line of argument the defect either exists in an alternative, excited configuration or is comprised of two components: the normal C_i defect responsible for the unconvertible part of the signal and a bistable defect of unidentified nature, which as it transforms between two configurations gives rise to the aforementioned behavior. We think that DLTS experiments carried out at temperatures below 80 K will bring new information for investigation of these points.

However, a more reasonable and physically plausible assumption is the following: From correlated photo-EPR and DLTS measurements[6] we know that the $E_v+0.28$-eV level of C_i is a single donor $(0/+)$. [The notation (i/j) means that the defect has a charge i when the level contains an electron and a charge j when empty.] From EPR studies[15] we also know that the B-V pair, at least in lowresistivity electron-irradiated material, introduces a donor state in the gap. The vacancy has also two donor levels, a double one $(+/2+)$ and a single one $(0/+)$.[16] In p-type material, cooling the sample in the absence of a reverse bias results in an injection of holes e^+ into the levels within the extent of the depletion region, which sets the defects in the positively charged state,

$$\mathrm{C}+e^+\rightarrow\mathrm{C}^+ ,$$

$$V+2e^+\rightarrow V^{2+} .$$

Thus, due to the negative U character of the vacancy in S_i,[16] the B-V pair under zero-bias conditions will be also positively charged,

$$B^-+V^{2+}\rightarrow\mathrm{B}\text{-}V^+ .$$

It is evident that under the above circumstances there is a small tendency for the C_i to annihilate the vacancy of the B-V pair by producing B-C pairs through a reaction between $(\mathrm{B}\text{-}V)^+$ and C^+ which has small chances to take place.

On the other hand, the effect of cooling the sample under reverse bias is to inject electrons which tend to neutralize the defects in the space-charge region of the diode,

$$2e^-+V^{2+}+\mathrm{B}\rightarrow V^0+\mathrm{B}^-=(\mathrm{B}\text{-}V)^- ,$$

$$e^-+\mathrm{C}^+\rightarrow\mathrm{C}^0 .$$

Thus the reaction

$$(\mathrm{B}\text{-}V)^-+\mathrm{C}^0\rightarrow V^0+(\mathrm{B}\text{-}\mathrm{C})^-$$

is now possible. As a result, the magnitude of the C_i peak height is smaller.

Consistent with this model is the fact that the $E_v+0.28$-eV signal does not show any variation of its amplitudes at room temperature where the B-V pair is not expected to be present.[9,15] The fact that the phenomenon also appears in pulled silicon, but with a lower intensity, may indicate that similar reactions take place between the C_i and a vacancy-related defect which also exhibits charge-dependent peak amplitudes.[17]

It is interesting to note that this model suggests that care is required in the interpretation of experimental data involving metastable defects. In future DLTS experiments carried out below 80 K, reactions similar to the above should be taken into account when trying to determine the equality of the concentrations of the peaks of the B-V complex between its two configurations.

ACKNOWLEDGMENTS

I am obliged to the Department of Physics of Reading University and particularly to Dr. P. C. Banbury for allowing me to use the research facilities there. I am grateful to Professor J. A. van Vechten for stimulating comments concerning the interpretation of the experimental data. The experiment was carried out while the author was on leave at Reading University, England.

---

[1] G. D. Watkins and K. L. Brower, Phys. Rev. Lett. **36**, 1329 (1976).

[2] R. C. Newman, *Infrared Studies of Crystal Defects* (Taylor and Fransis, London, 1973), p. 124.

[3] L. C. Kimerling, P. Blood, and W. M. Gibson, in *Defects and Radiation Effects in Semiconductors,* Proceedings of the International Conference on Radiation Effects in Semiconductors, Nice, 1978, edited by J. H. Albany (IOP, London, 1978), p. 273.

[4] R. D. Harris and G. D. Watkins, in *Proceedings of the 13th International Conference on Defects in Semiconductors,* edited by L. C. Kimerling and J. M. Parsey, Jr. (AIME, New York, 1985), p. 799.

[5] L. C. Kimerling, in *Radiation Effects in Semiconductors,* Proceedings of the International Conference on Radiation Effects in Semiconductors, Dubrovnik, 1976, edited by N. B. Urli and J. W. Corbett (IOP, Bristol, 1977), p. 221.

[6] Y. H. Lee, L. J. Cheng, L. J. Gerson, P. M. Mooney, and J. W. Corbett, Solid State Commun. **12**, 109 (1977).

[7] L. W. Song, B. W. Benson, and G. D. Watkins, Phys. Rev. B **33**, 1452 (1986).

[8] C. A. Londos, Phys. Status Solidi A **92**, 609 (1985).

[9] S. K. Bains and P. C. Banbury, J. Phys. C **18**, L109 (1985).

[10] D. V. Lang, in *Thermally Stimulated Relaxation in Solids,* Vol. 37 of *Topics in Applied Physics,* edited by P. Braunlich (Springer-Verlag, Berlin, 1979), p. 93.

[11] B. Hamilton, A. R. Peaker, and D. R. Wight, J. Appl. Phys. **50**, 6373 (1979).

[12] G. D. Watkins, Phys. Rev. B **12**, 4383 (1975).

[13] J. R. Troxell and G. D. Watkins, Phys. Rev. B **22**, 921 (1980).

[14] J. L. Benton and M. Levinson, in *Defects in Semiconductors II,* edited by S. Mahajan and J. W. Corbett (North-Holland, New York, 1983), p. 95.

[15] G. D. Watkins, Phys. Rev. B **13**, 2511 (1976).

[16] G. D. Watkins and J. R. Troxell, Phys. Rev. Lett. **44**, 593 (1980).

[17] C. A. Londos and P. C. Banbury, J. Phys. C (to be published).