PHYSICAL REVIEW B VOLUME 35, NUMBER 14 15 MAY 1987-I

Divacancy production in low-temperature electron-irradiated silicon

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

(Received 22 December 1986)

We report deep-level transient spectroscopy studies on the divacancy formation in electron-bombarded silicon at 80 K. Samples irradiated to a dose $D_1 = 3.5 \times 10^{16}$ e^-/cm^2 and using a beam current $i_1 = 0.33$ $\mu\mathrm{A/cm}^2$ give rise to an unstable peak seen to anneal out rapidly below 150 K. The center responsible for this peak seems to act as an intermediate step in the formation of at least a fraction of the neutral divacancies. Under conditions of irradiation with dose $D_2 = 1.7 \times 10^{16}$ e^-/cm^2 and beam current $i_2 = 0.20$ $\mu\mathrm{A/cm}^2$ neither the intermediate defect nor the neutral divacancy signal appears in the spectrum. Instead, a divacancy-related $E_V + 0.13$ eV level emerged. An interpretation of the data is attempted in terms of a model postulating charge-state-dependent metastable structures.

INTRODUCTION

An understanding of defects must necessarily include an understanding of their formation and the kinetics of their motion in a crystal. The silicon divacancy has been extensively studied by using different experimental techniques. However, there are still some unclear points concerning the production mechanisms and the influence of the self-interstitial and of different impurities on its formation.

The primary damage event in silicon after 1.5-MeV electron bombardment mainly consists of Frenkel pairs (i.e., a vacancy and an interstitial). However, there is experimental evidence that divacancies can be created by a direct collision process during the electron irradiation when two adjacent atoms are knocked out of the lattice.[1,2] It is also well known that divacancies are formed as secondary events via agglomeration of two single vacancies.

In this work we present experimental data supporting the existence of a center acting as an intermediate step in the formation of a fraction of the divacancies at low temperatures, prior to the onset of the vacancy migration. The correlation of its nature with aggregates of self-interstitial atoms around a divacancy may contribute to a better comprehension of the behavior of the elusive silicon interstitial.

EXPERIMENT

We used Schottky diodes fabricated from boron-doped pulled silicon wafers of ⟨100⟩ orientation with a nominal resistivity of 3—5 Ω cm. The specimens, mounted inside a liquid-nitrogen cryostat, were subjected an irradiation of 1.5-MeV electrons from a Van der Graaf accelerator, under different dose and beam current conditions. Deep level transient spectroscopy (DLTS) studies and annealing measurements were performed *in situ* by using a capacitance spectrometer similar to that described by Lang.[3] During the measurements a 5-V reverse voltage was applied while the filling-pulse amplitude was 5.8 V to compensate for the built-in voltage of the diode.

RESULTS AND DISCUSSION

Detailed observations of the capacitance transient spectra of silicon under electron bombardment at different irradiation conditions have brought to light some interesting information concerning the divacancy formation at low temperatures.

Figure 1 displays the DLTS spectrum below 155 K, produced under conditions of dose $D_1 = 3.5 \times 10^{16}$ e^-/cm^2 and beam current $i_1 = 0.33$ $\mu\mathrm{A/cm}^2$ (a) immediately after the irradiation (solid curve), (b) about half an hour later (dashed curve), and (c) after the annealing out of the vacancy (dotted curve). We label the peaks of curve (a) as H_1, H_2, and H_3. Peak H_1 can be only partially seen even with the pair of the fastest available rate windows operating at 100 and 2500 s^{-1}, making impossible any accurate determination of its activation energy. From its position in the spectrum, its relative concentration and its annealing behavior, H_1 is believed to be the vacancy. Peak H_2 is seen only in the first scan [curve (a)] after the irradiation. At the end of this scan around 155 K the specimen was quenched to 80 K. In the next scan [curve (b)], with the temperature ramping upwards, H_2 has been significantly reduced to a weak signal H_2' which remains stable in all the successive temperature cyclings. The reduction of H_2 is accompanied by a simultaneous enhancement of H_3, while the loss of H_2 is equal to the gain of H_3. We found an activation energy of $E_v + 0.15$ eV for H_2' and of $E_v + 0.19$ eV for H_3. From the position on the temperature axis, the energy value, the annealing behavior and comparisons with previous reports, H_3 is attributed to the neutral charge state of the divacancy. However, the determination of the activation energy in this work gives a value ($E_v + 0.19$ eV) which is distinctly less than that previously reported[2,4] around $E_v + 0.23$ eV. Curve (c) was taken after an anneal of the sample at 215 K for 40 min under zero-bias conditions. Peak H_1 has

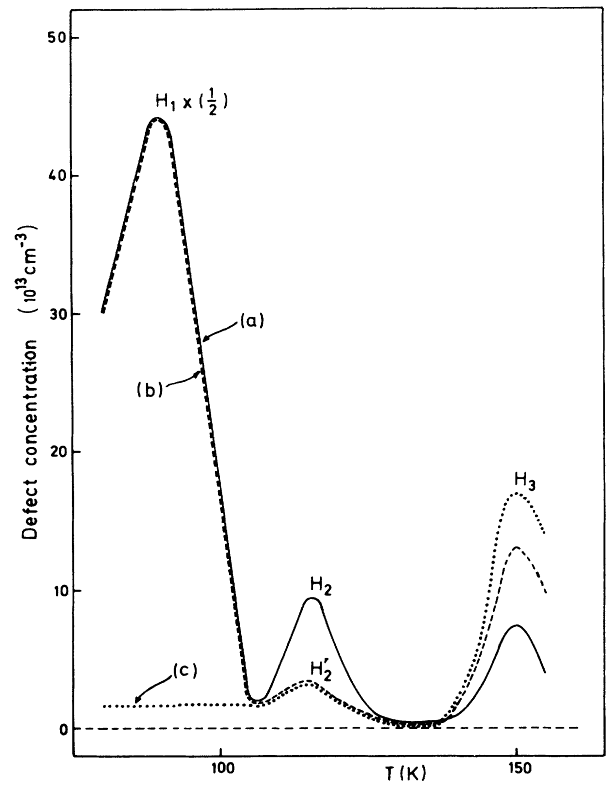

FIG. 1. The DLTS spectrum of boron-doped pulled silicon, $\rho = 3-5\ \Omega$ cm, after 1.5-MeV electron irradiation at 80 K at a dose $D_1 = 3.5 \times 10^{16}\ e^-/\text{cm}^2$ and a beam current $i_1 = 0.33\ \mu\text{A/cm}^2$ (a) immediately after the irradiation (solid curve), (b) about half an hour later (dashed curve), and (c) after the annealing out of the vacancy (dotted curve).

disappeared as expected for the vacancy and peak H_3 has a further increase which is consistent with the divacancy identification.

Let us consider peak H_2. It is clear that H_2 acts as an intermediate step in the formation of some of the divacancies. The available DLTS data are admittedly insufficient to provide the basic information required to draw definite conclusions about the nature and the exact kinetics of the microscopic process involved in the observed annealing stage. However, the simplicity of the phenomenon and the low temperature where it appears stimulates some warranted speculations. At first the fact that H_3 increases by the same amount and simultaneously with the diminution of H_2 [curve (b)] indicates that only one process occurs during the annealing stage and that this process may involve divacancies. It seems likely that H_2 releases divacancies after dissociation at a certain temperature which in turn causes the increase of the H_3 signal. Secondly the low temperature where this annealing stage happens places severe restrictions on the variety of the different structures which may be suggested as candidates concerning the nature of H_2. Infrared absorption measurements[5] on silicon before irradiation have revealed the presence of O_i, C_s, B_s atoms, and even of O_i-O_s pairs. After the liquid-nitrogen irradiation the following structures are expected to exist: V, Si, O_i, C_s, C_i, B_s, B_i, V_2, and O_i-C_s. Since, among them, only the Si_i is mobile at these low temperatures, one may also expect the presence of pairs like O-Si_i, C-Si_i, and B-Si_i. Finally, because of the distribution in energy received in the primary collision and because of the fluctuation in the positions of the neighboring atoms of the lattice, we may consider the following processes in connection with the V_2 formation.

(A) The fast electron knocks out an atom from a lattice site. This atom in turn may have enough energy to produce subsequent secondary displacements. It knocks out a second adjacent atom leading to the formation of a normal divacancy. However, the smaller than expected activation energy determined in our case may indicate the presence of an unknown component, presumably a silicon interstitial trapped in the vicinity of the divacancy. This means that the aforementioned component holds a somehow loose bond to the divacancy, and this fact slightly affects its energy position in the gap. This fraction of the divacancies give rise to peak H_3 [curve (a)].

(B) Either one or both of the dislodged silicon atoms are not displaced far from the divacancy. This may lead to a close-spaced divacancy-interstitial arrangement which in both cases "lock," the divacancy configuration. As a result the crystal field is strongly perturbed around this structure. The divacancy is highly distorted and the surrounding lattice as well. Such a situation may have a big effect on the behavior of a defect. More specifically it may affect the energy position in the gap, the stability of one site over another, its dependence on charge state and the relative stability of the charge states. Presumably the activation energy for motion in the lattice is also affected.[6] In our case the result appears in the spectrum with the emergence of an unstable peak H_2 [curve (a)]. The "locking" persists until thermally annealing below 155 K. In other words, as the temperature increases the barrier height for dissociation of the structure is surmounted resulting in the diminution of H_2 and the enhancement of H_3 [curve (b)]. The latter is due to the liberating divacancies. The released silicon interstitials traveling in the lattice are captured by one of the impurities present: carbon, boron, and predominantly oxygen.

An alternative possibility for the case of one silicon interstitial-divacancy structure is the previously suggested paired semivacancy configuration[7] where two adjacent lattice sites are unoccupied and a silicon atom occupies the interstitial position midway. We should also notice that apart from the normal divacancy configuration (i.e., two vacancies on adjacent sites) a V-Si-Si-V configuration (i.e., two vacancies separated by two occupied lattices sites) has been proposed as an energetically possible candidate for the defect responsible for the NL_{11} EPR spectrum.[8] It was found that the latter configuration is metastable with a tendency to move the vacancies to the normal divacancy configuration. Although such a structure (which is a simple member of a family of defects termed sponge defects[9]) comprising two remotely coupled vacancies has so far evaded experimental observation, there is no impediment which presumably prevents it forming.

The intriguing possibility of another charge state of the vacancy which in p-type silicon gives rise to peak H_2 and anneals out below 150 K forming divacancies via agglomeration should be considered with caution since H_2 appears only in pulled silicon as mentioned below. An even stronger argument against such an assumption is the fact that a migration of isolated vacancies in oxygen-rich material should lead to the formation of V-O pairs. The V-O pair gives rise to a well-known $E_c-0.17$ eV level which has not been detected in our minority-carrier trap spectroscopy (MCTS) spectra when the samples are subjected to temperature cyclings below 150 K. However, a signal from the O-V pair appeared in our spectrum after the annealing out of the H_1 peak attributed to the vacancy. For similar reasons we can also rule out the possible formation of vacancy-silicon interstitial pairs separated by a few lattice spacings. Finally we cannot exclude the assumed formation of a structure comprising an unidentified partner for the divacancy or the nucleation of more than two silicon agglomerates at random sites around a divacancy.

An increase in the divacancy concentration upon heating from 140 K and below has been reported[10] in low-temperature neutron-irradiated silicon. It was suggested that a defect cluster was formed comprising a vacancy-rich region which begins to reorder as the temperature increases. It is obvious that we cannot propose a similar interpretation since electrons of 1.5-eV energy are unlikely to produce clusters and disordered regions.

(C) After the beginning of the vacancy migration, divacancies can be formed by the interaction of two single vacancies. This results in an increase of the initial concentration of the divacancies as reflected in peak H_3 [curve (c)]. At this stage oxygen and boron, which are known traps for the vacancies, compete with the divacancy formation.

The situation, however, appears quite different if we change the conditions of irradiation. Figure 2 displays the DLTS spectrum resulting after electron irradiation to a dose of $D_2=1.7\times10^{16}$ e^-/cm^2 and a beam current of $i_2=0.20$ $\mu\mathrm{A/cm}^2$. The time of irradiation was about the same as under the (D_1,i_1) conditions. Two main differences were observed in comparison with Fig. 1. The intermediate defect H_2 was absent and the divacancy level $E_v+0.19$ eV as well. Instead, another peak H_4 was emerged in the spectrum giving an energy level $E_v+0.13$ eV. A study of the latter gave the following observations.

(i) Its amplitude increases around 7% when the vacancy migrates [Fig. 2, curve (c)].

(ii) The peak resists an annealing at 470 K for 60 min.

(iii) The spectrum displays the same peaks for samples subjected to irradiation conditions $D=1.7\times10^{16}$ e^-/cm^2, $i=0.10\,\mu\mathrm{A/cm}^2$.

(iv) The level $E_v+0.13$ V is absent in float-zone silicon material subjected to similar electron bombardment.[11]

(v) Its hole-capture cross section estimated with the pulse width variation method gave a value around $\sim10^{-18}$ cm^2, which indicates that the center is mostly at a positive charge state. However, this low value has been probably influenced by a strong edge-layer effect. The applied reverse bias (5 V) and the filling pulse amplitude (5.8 V) do not exclude such a possibility. This is further supported from the obtained poor linearity in the graphical representation of the log of the DLTS output against the pulse width.

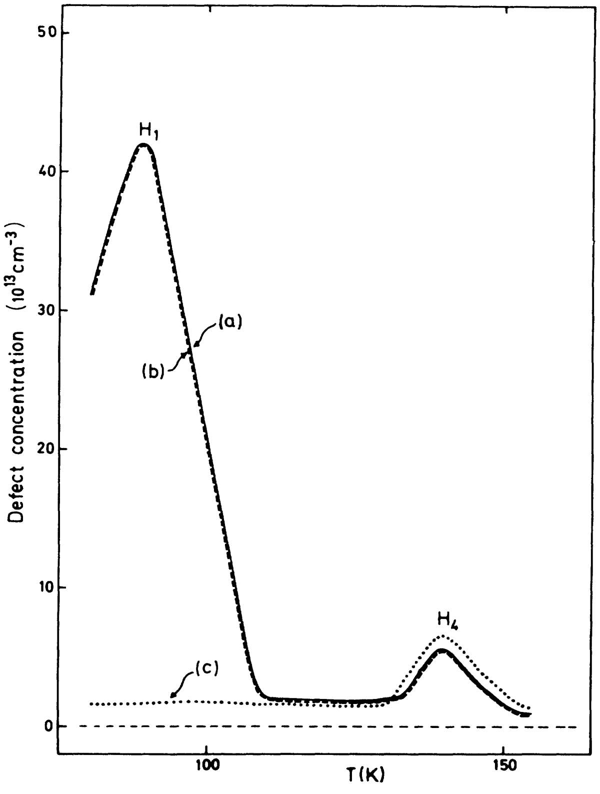

FIG. 2. The DLTS spectrum of boron-doped, pulled silicon, $\rho=3-5$ Ω cm, after 1.5-MeV electron irradiation at 80 K at a dose $D_2=1.7\times10^{16}$ e^-/cm^2 and a beam current $i_2=0.20$ $\mu\mathrm{A/cm}^2$: (a) and (b) The first and the second scan after the irradiation are the same (solid and dashed curve). (c) A scan after the annealing out of the vacancy (dotted curve).

Using thermally stimulated capacitance measurements, Brabant *et al.* have reported[12] the presence of a level (0.12 ± 0.02) eV above the valence band after 1.5-MeV liquid-helium electron irradiation of boron-doped silicon to a dose of 5×10^{15} e^-/cm^2. In those studies the behavior of the level in general, apart from the activation energy value, fits with that of the neutral divacancy. From the activation energy, the annealing behavior and the similarity of the conditions of irradiation, we are inclined to believe that the level in Ref. 12 and that responsible for H_4 are the same. In a preliminary assignment we have correlated the $E_v+0.13$ eV level with an oxygen-dependent, divacancy related center. The possibility of structure like V-C-C-V, V_2B, etc., cannot be excluded, although the relative high production rate of H_4 ($\sim3.4\times10^{-3}$ cm^{-1}) argues against such identifications because of the low mobilities of all the partners at these low temperatures.

Evidently, the creation and the stability of a defect structure depends on the temperature and the conditions of irradiation mainly in cases when more than one charge state exist. The properties of the defect are also expected to depend upon the type of the material (n or p) and the impurities present. By following the considerations of Wertheim[13] and those of Mackay and Klontz[14] about metastable close pairs of vacancies and interstitials we propose the formation of a charge-state-dependent, close-spaced divacancy-silicon interstitials configuration in order to explain the data.

Under conditions of irradiation (D_1,i_1), where either the dose or the beam current or both are higher than certain critical values, the charge state of some of the partners favors the formation of a short-lived thermally unstable structure which gives rise to the peak H_2. The released self-interstitials are captured mainly by oxygen and other impurities while the liberated divacancies contribute in the increase of H_3. It is necessary to notice here that the opposite phenomenon has been reported in n-type silicon subjected to similar conditions of liquid-helium irradiation where an annealing stage has been found below 140 K.[15] At this stage most of the divacancies, in particular the nonreorientable divacancies, disappear. This has been interpreted by the onset of the migration of two silicon interstitial atoms trapped nearby the divacancy which at $T \sim 140$ K become mobile, pop back, and destroy the divacancy by annihilation. In contrast to the situation in n-type silicon, it seems that such a process is prevented in p-type silicon.

Under conditions of irradiation (D_2,i_2) with either the dose or the beam current or both smaller than the critical values, the charge states of the partners are either unfavorable to the formation of H_2, or H_2 is now so unstable that it dissociates rapidly below the temperature where it can be detected by DLTS. Instead, another divacancy-related configuration much more stable is created, giving rise to the $E_v+0.13$ eV level in the gap. The exact identity of the latter is unknown.

The role of oxygen at these low temperatures seems essential, not restricted only to that of a trap for the interstitials. It certainly influences the formation of the divacancy in different ways. Floating-zone silicon of similar resistivities subjected either (D_1,i_1) or (D_2,i_2) conditions of irradiations has shown neither the intermediate defect H_2 of Fig. 1 nor the peak H_4 of Fig. 2. In both cases the spectra below 155 K, when the 2500 sec^{-1} rate window was operated, gave two dominant peaks: the vacancy and the divacancy.[11,16]

It is evident that our results, based solely on DLTS experiments, are inadequate to justify a conclusive model. In this respect, the above model about a close-spaced, charge-state dependent, divacancy-silicon interstitial configuration should be regarded as tentative pending further investigation.

ACKNOWLEDGMENT

I am obliged to the Physics Department of Reading University and particularly to Dr. P. C. Banbury for providing their research facilities to carry out the above experiment.

---

[1] J. W. Corbett and G. D. Watkins, Phys. Rev. Lett. **7**, 314 (1961).

[2] J. W. Corbett and G. D. Watkins, Phys. Rev. **138**, 556 (1965).

[3] D. V. Lang, J. Appl. Phys. **45**, 3023 (1974).

[4] L. C. Kimerling, Radiation Effects in Semiconductors, Dubzovnik, 1976 [Inst. Phys. Conf. Ser. **31**, 221 (1977)].

[5] R. C. Newman, Rep. Prog. Phys. **45**, 1163 (1982).

[6] L. C. Kimerling, H. M. De Angelis, and J. W. Diebold, Solid State Commun. **16**, 171 (1975).

[7] B. J. Masters, Solid State Commun. **9**, 283 (1971).

[8] E. G. Sieverts and J. W. Corbett, Solid State Commun. **43**, 41 (1982).

[9] J. Hornstra, Phillips Research Laboratory Report No. 3497, 1959 (unpublished).

[10] C. E. Barnes, *Radiation Effects in Semiconductors*, edited by J. W. Corbett and G. D. Watkins (Gordon and Breach, Albany, 1970), p. 203.

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

[12] J. C. Brabant, M. Pugnet, and M. Brousseau, Radiation Effects in Semiconductors, Dubzovnik, 1976 [Inst. Phys. Conf. Ser. **31**, 200 (1977)].

[13] G. K. Werthein, Phys. Rev. **115**, 568 (1959).

[14] J. W. Mackay and E. E. Klontz, J. Appl. Phys. **30**, 1269 (1959).

[15] R. D. Harris and G. D. Watkins, *Thirteenth International Conference on Defects in Semiconductors, Coronado, 1984*, edited by L. C. Kimerling and J. M. Parsey (Metallurgical Society, AIME, Warrendale, Penn., 1985), p. 799.

[16] C. A. Londos (unpublished data).