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CARBON INTERSTITIAL IN ELECTRON-IRRADIATED SILICON*

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Using photo-EPR measurements on the Si-G12 spectrum in electron-irradiated silicon, it is shown that the carbon interstitial, already known to form a ⟨100⟩-interstitialcy, also gives rise to an electrical level at $(E_v + 0.30)$ eV. We estimated the hole capture cross section of the defect to be $\sigma_p \geqslant 10^{-17}$ cm^2, using deep-level transient spectroscopy.

A CARBON interstitial in electron-irradiated silicon has been studied in detail by optical[1] and electrical[2] measurements. The infrared studies[1] observed a considerable increase of the divacancy concentration in carbon-doped silicon, leading to the tentative conclusion that the carbon impurity is an effective trap for the self-interstitial and prevents the self-interstitial from recombining with a vacancy Thus, the C(1) center (the 921 and 930 cm^{-1} bands), which is unstable near room temperature and has a C^{13} isotope effect, must arise from a carbon–silicon interstitial pair in a C_{3v}- or D_{3d}-symmetric configuration [3] Also, Hall effect and photoconductivity measurements[4] for *p*-type silicon revealed a defect at $(E_v + 0\ 25)$ eV, which anneals out at room temperature and was thought to be due to a carbon center [2]

Recently, Watkins and Brower[5] identified a carbon interstitialcy in silicon from their EPR studies for the G12 spectrum.[6] The G12 center was produced by electron irradiation at a low temperature (100–300 K) and gives rise to the C^{13} hyperfine structure. They reported that a carbon, originally at a substitutional site, forms a ⟨100⟩-interstitialcy by trapping a mobile Si-interstitial, and that upon annealing at 350 K the defect breaks up and the C-interstitial can be retrapped by another substitutional carbon, forming a $[C_S–C_I]$ pair (the G11 spectrum).[7] The annealing temperature of the G12 center is consistent with that of the C(1) center in the infrared results, but the G12 center has C_{2v} symmetry In this communication, we report our new results from a photo-EPR experiment and Deep-Level Transient Spectroscopy (DLTS),[8] showing that a positive charge state of the carbon interstitial results in a hole trap at $(E_v + 0.30)$ eV

From an ingot of a *p*-type crystal, samples were cut to a size of $(0.2 \times 0.2 \times 0\ 2\ \text{cm}^3)$ along ⟨110⟩ for the EPR measurement and into a thin wafer to fabricate a diode for the DLTS measurements The EPR samples were irradiated at 100 K with 1.5 MeV electrons at the fluence 10^{17} e/cm^2 For the DLTS samples, we used various electron energies between 0.8 and 2.0 MeV and the fluence ranged from 10^{15} to 10^{17} e/cm^2 The samples were kept at 300 K during irradiation and then stored at 77 K after irradiation

We resolved the G12 spectrum not only in B-doped floating-zone grown silicon, but also in B-doped crucible grown and Al-doped floating-zone silicon, apparently because of a natural carbon impurity in the samples The G11 spectrum was not observed in all the samples we studied. Figure 1 shows three G12 spectra observed in B-doped floating-zone silicon with $\rho = 12\ \Omega$-cm the top spectrum was taken before photo-illumination, and the middle and bottom ones were taken while illuminating with monochromatic light of 1 2 and 1.5 μm, respectively. We observe that the photo-response of G12 depends on the initial resistivity of the sample, i.e in a 12 Ω-cm sample, the G12 intensity increases upon photo-illumination for $\lambda < 1\ 5\ \mu$m, as shown in Fig. 1, while in a 1.0 Ω-cm sample irradiated to the same electron fluence, the G12 intensity decreases for $\lambda = 1.2$–$4\ 0\ \mu$m Since the G7 spectrum[9] (a negative charge state of the divancy) at $(E_c - 0\ 40)$ eV appears in the high resistivity sample without illumination, the Fermi level moved to near (or above) the middle of the band gap. Thus the G12 centers were mostly at the neutral charge state, and electronic photo-excitation from the neutral G12 center to the conduction band results in the population increase at a positive charge state On the other hand, in the low resistivity sample, the G6 spectrum,[9] due to a positive charge state of the divacancy at $(E_v + 0\ 25)$ eV,

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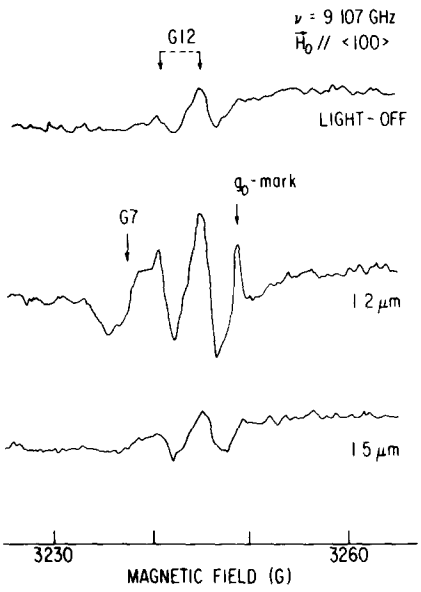

Fig 1. EPR signal of Si-G12 at $T = 77$ K. The orientational degeneracy results in two resonance lines as $\mathbf{H}_0 \| \langle 100 \rangle$. The G12 shows a strong passage effect which causes the reverse phase at the r.f. power 8 2 mW with respect to the G7 signal. The photo-response was maximum at $\lambda = 1\ 2\ \mu$m and ceases at $\lambda = 1\ 5\ \mu$m (The g_0 mark is for the free electron g-value).

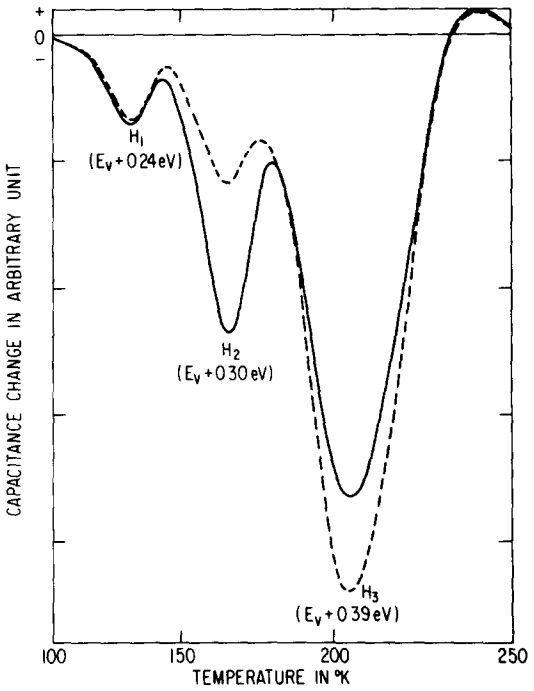

Fig. 2. Typical majority trapping spectra of DLTS measurements on 2 Ω-cm p-type silicon diodes, irradiated with 0.8 MeV electrons at 25°C to the fluence of 10^{17} e/cm^2 The solid line represents a spectra before annealing and the dashed line is after annealing at 56°C for 3 min

was simultaneously observed with G12, indicating that the Fermi level in this sample should be near 0.25 eV from the valence band Therefore, the G12 centers were mostly at a positive charge state and a hole excitation from the defect level to the valence band was a dominant effect in the photo-response, causing the decrease in the G12 intensity Based on the intensity variation of G12 as a function of the incident photon energy in both samples, we estimate the electrical level for a positive charge state of the G12 center to be $[E_v + 0\ 30\ (\pm\ 0.02)]$ eV, in rough agreement with the prediction based on the photoconductivity measurement [4]

Figure 2 shows a typical DLTS spectra measured in a 2 Ω-cm diffused diode following 0 8 MeV electron irradiation When the temperature is scanned from 77 to 300 K, three dominant peaks (H_1, H_2 and H_3) appear, each of which represents a thermally excited hole emission from a particular defect to the valence band We observed those three peaks in diffused diodes fabricated from the same ingots we used for our EPR measurement We determine the defect electrical levels of H_1, H_2 and H_3 to be 0 24, 0 30 and 0.39 eV, respectively, from the valence band (with an error range of ± 0 02 eV) These three centers are the most dominant defects observed in p-type silicon of various resistivities irradiated at 300 K with 1.0 MeV electrons Because of its annealing behavior, the H_1 peak was attributed to a positive charge state of the divacancy which is not our concern in this report We carried out detailed isothermal annealing for the H_2 peak at 36, 46, 56 and 61 C and found that, while the H_2 peak diminishes during annealing, the H_3 peak grows as shown in Fig. 2. The activation energy for the defect recovery is estimated to be 0.8 (± 0 1) eV with the pre-exponential frequency of $\sim 10^{10}$ sec^{-1} This is consistent with the activation energy (0 88 eV) for a defect reorientation of the G12 center which Watkins and Brower[5] derived from the recovery of stress alignment Therefore, we attribute the H_2 peak to the G12 center, i e. the carbon–silicon interstitial pair The hole capture cross-section of the H_2 peak was estimated to be $\geqslant 10^{-17}$ cm^2, supporting our previous assumption that the G12 center is mostly at the neutral charge state, when the Fermi level lies near the middle of the band gap Also, Kimerling independently observed the H_2 peak[10] with $\sigma_p = 7 \times 10^{-18}$ cm^2 He suggested that the carbon interstitial causes the H_2 peak. Since there are a number of defects such as the boron interstitial[11] and the oxygen–silicon interstitial pair[12] which become mobile around room temperature, the DLTS technique alone is not sufficient to identify a microscopic defect Using both EPR and DLTS, we obtain more profound results (1) both the H_2 peak and the G12 spectrum appear in the samples fabricated from the same ingots, (2) our EPR

measurement for the G12 defect level is consistent with that of the H_2 peak, and (3) the activation energy for the defect recovery is in good agreement with the EPR result of G12. These results may be regarded as strong evidence for the identification of the H_2 peak.

All the available results from the different experimental techniques, i.e the Hall effect, photoconductivity, infrared, EPR and DLTS, are consistent with one another, except for the symmetry assignment of the C(1) band in the infrared study. Since the sample condition in the i r study seems close to our 12 Ω-cm sample, the C_{3v}-symmetry could be for the neutral charge state We should point out, however, that the i.r results by Bean and Newman[3] could be interpreted as either C_{3v} or D_{2d}, and that a localized vibrational mode of the [C–Si] interstitialcy in C_{2v} would appear to be in D_{2d} because of the accidental degeneracy in the x- and y-directions Further stress study for the C(1) band is required to answer conclusively on this point

As illustrated in Fig. 2, the H_3 peak at $(E_v + 0.39)$ eV emerges at room temperature, while the H_2 peak diminishes The H_3 peak anneals out at 400°C. Two capture cross sections are measured for the H_3 peak, $\sigma_p(1) = 2 \times 10^{-16}$ cm^2 and $\sigma_p(2) = 7 \times 10^{-19}$ cm^2, suggesting that the H_3 peak may be associated with two different defects This was further supported by the fact that $\sigma_p(2)$ changes to 3×10^{-17} cm^2 after the 300°C annealing, while $\sigma_p(1)$ is persistent throughout the temperature range of annealing Kimerling[10] also observed a peak at $(E_v + 0\ 33)$ eV which has the hole capture cross-section of 8×10^{-17} cm^2 and anneals out at 400°C, similar to the H_3 peak, he speculated that this peak is due to the $[C_S–C_I]$ pair (the G11 EPR spectrum) [7] We note that the G11 center anneals at 300°C, which contradicts his identification Recently, we identified the [vacancy–carbon–oxygen] complex[13] which gives rise to the G15 spectrum at a positive charge state at $(E_v + 0\ 30)$ eV and anneals at 400°C. Since the annealing behavior and defect electrical level of G15 are very similar to Kimerling's values, $\sigma_p(1)$ may be attributed to the [V + C + O] complex and $\sigma_p(2)$ to the $[C_S–C_I]$ pair, but they require more information to confirm the correlation The DLTS results clearly indicate a breaking-up of the carbon interstitial from the [C–Si] pair at a room temperature and a recombination with other impurities such as carbon or oxygen, as observed by EPR. However, the loss in the H_2 peak is almost twice as large as the gain in the H_3 peak, suggesting that the carbon interstitial may go to some other unknown defects as well, as observed in the infrared studies [12] Since the H_1 peak (the divacancy) does not change below 100°C, the possibility of forming a [C–V] pair[14] by combining with $[V_2]^+$ seems to be small, probably due to the Coulomb repulsion

In conclusion, the carbon–silicon interstitial pair results in a defect electrical level at $(E_v + 0\ 30)$ eV which plays as an effective trap for the free carrier with the hole capture cross section of $\sim 10^{-17}$ cm^2

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