

# Identification of a bistable defect in silicon: The carbon interstitial-carbon substitutional pair

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By using a combination of deep level transient spectroscopy (DLTS) and electron paramagnetic resonance techniques applied to samples of varying compositions, we identify the bistable defect at  $E_c - 0.17$  eV in irradiated  $n$ -type silicon as a carbon interstitial-carbon substitutional pair. It arises upon annealing of interstitial carbon, which is also the precursor to a remarkable recently discovered four-level multistable defect which we now tentatively identify as a carbon-phosphorus pair. We demonstrate a new simple method for distinguishing the bistable carbon-carbon pair defect from the oxygen-vacancy pair under the same DLTS peak.

The association of an  $E_c - 0.17$  eV defect level observed in the deep level transient capacitance spectroscopy (DLTS) spectrum of irradiated  $n$ -type silicon with the oxygen-vacancy pair (O-V)<sup>1</sup> has long been well established.<sup>2</sup> Several years ago, a bistability was reported involving the  $E_c - 0.17$  eV level where an alternative configuration with energy level at  $E_c - 0.10$  eV could be observed under special experimental conditions.<sup>3</sup> This phenomenon has been variously interpreted to be either an intrinsic feature of the oxygen-vacancy pair defect,<sup>4</sup> or a slightly altered oxygen-vacancy pair involving an additional nearby impurity.<sup>3,5</sup>

In this letter, we report for the first time results of DLTS studies in samples with low oxygen concentration along with correlative electron paramagnetic resonance (EPR) studies to independently determine the separate defect species present. From these results we find that there are actually two distinct defects that give rise to the DLTS peak at  $E_c - 0.17$  eV. One is the O-V pair which displays no bistable properties. The other has bistable properties and contains neither oxygen nor vacancies. We demonstrate that it is the single acceptor state ( $-/o$ ) of a carbon interstitial-carbon substitutional pair ( $C_i-C_s$ ).

The samples used for study are listed in Table I. All were floating-zone grown (low oxygen) but had varying carbon and donor concentrations and chemical donor species. The carbon and oxygen concentrations were estimated by infrared (IR) absorption measurements of their local mode spectra. Although undetectable by IR spectroscopy ( $<2 \times 10^{16} \text{ cm}^{-3}$ ), the oxygen content of these samples can still be comparable to the dopant concentration and effective in capturing vacancies. The intensity of the O-V EPR signal after irradiation serves as a reliable measure of this background oxygen content, which is found to vary from sample to sample as seen in Table I.

The diode junctions were fabricated with a Schottky barrier contact to avoid additional oxygen incorporation into the junction. Electron irradiations were performed at 2.5 MeV from a van de Graaff accelerator at room temperature. The samples were mounted on an air-cooled aluminum block and irradiation was performed with a low beam current ( $<4 \mu\text{A}/\text{cm}^2$ ) to avoid sample temperature rise during

the irradiation. Conventional DLTS techniques were used with a double boxcar analyzer. EPR studies were performed at 14 GHz and at  $T \sim 20\text{--}40$  K on larger bulk samples. The diode wafers and EPR samples were cut from adjacent regions of each boule.

Immediately following room-temperature irradiation, a level at  $E_c - 0.10$  eV was observed in all samples for which the carbon concentration was  $\geq 10^{16} \text{ cm}^{-3}$  (listed in Table I as "precursor"  $E_c - 0.10$  eV). A level at  $E_c - 0.17$  eV, on the other hand, was seen only in sample 1. In the companion EPR studies, O-V pairs were found to be present also in sample 1 only.

The precursor giving rise to the  $E_c - 0.10$  eV level is not stable at room temperature. When it disappears upon annealing at 300–350 K, the DLTS peak at  $E_c - 0.17$  eV increases in intensity as does a peak at  $E_c - 0.30$  eV, which is associated with a newly discovered four-level multistable defect, as previously reported.<sup>6–8</sup> The annealing results for sample 1 are shown in Fig. 1. For this sample, with high carbon and low phosphorus concentrations, most of the conversion is to the  $E_c - 0.17$  eV level. (See Fig. 2 of Ref. 6, which was performed on a wafer from a different source and with higher phosphorus concentration, for the reverse case.) EPR studies reveal no increase in the O-V pairs in any of the samples during this anneal.

We find that prior to this anneal, the  $E_c - 0.17$  eV level displays no bistability. The component that emerges upon annealing, however, is bistable. In Fig. 1 and in Table I, we have therefore separated the bistable  $E_c - 0.17$  eV component from the initial normal component.

The stable and bistable components can be separately determined with DLTS in two ways. (1) When cooled under reverse bias to  $<50$  K, both the  $E_c - 0.10$  eV and the  $E_c - 0.17$  eV levels of the bistable defect are observed in the subsequent DLTS scan.<sup>4,5</sup> Cooled under zero bias, only the  $E_c - 0.17$  eV level is observed. The intensity of the  $E_c - 0.10$  eV peak provides therefore a direct measure of the bistable component. (2) By simply monitoring the amplitude of the  $E_c - 0.17$  eV peak versus majority-carrier pulse width in a normal DLTS experiment, we find that the two components can also be separated. As shown in Fig. 2, the

TABLE I. Sample composition and defect production rates. All samples were floating zone grown with  $[O] \leq 2 \times 10^{16} \text{ cm}^{-3}$ .

| Sample | Concentration<br>( $\times 10^{16} \text{ cm}^{-3}$ ) |        | O-V<br>$E_c - 0.17 \text{ eV}$ | Production rate ( $\text{cm}^{-1}$ )              |  |   |
|--------|---|--------|--------------------------------|---|--|---|
|        | Dopant  | Carbon |                                | Precursor<br>$E_c - 0.10 \text{ eV}$<br>( $C_i$ ) | Bistable<br>$E_c - 0.17 \text{ eV}$<br>( $C_i-C_s$ ) | Multistable<br>$E_c - 0.30 \text{ eV}$<br>( $C_i-P_s$ ) |
| 1      | P~0.1   | 10     | 0.006                          | 0.018   | 0.016  | 0.0018  |
| 2      | P~0.6   | 2.4    | $< 10^{-4}$                    | 0.016   | 0.008  | 0.0036  |
| 3      | Sb~1  | 1.5    | $< 10^{-4}$                    | 0.010   | 0.004  | ...   |
| 4      | P~0.9   | <1     | $\leq 10^{-4}$                 | $\leq 0.0003$                                     | $\leq 10^{-4}$                                       | 0.0006  |

amplitude matches the form

$$n = n_0 + (n_\infty - n_0) [1 - \exp(-t/\tau)],$$

where the pulse-width-independent contribution  $n_0$  measures the concentration of O-V pairs, known to have a very high capture cross section,<sup>3</sup> and  $(n_\infty - n_0)$  measures the bistable defect concentration. The exponential dependence reflects the conversion rate of the bistable defect after electron capture from its  $E_c - 0.10 \text{ eV}$  configuration to the  $E_c - 0.17 \text{ eV}$  configuration when negatively charged. The time constant  $\tau \sim 2.2 \times 10^{-4} \text{ s}$  that we measure at  $T \sim 86 \text{ K}$  matches well the results for this conversion as reported by Jellison.<sup>3</sup> (The characteristic time for return to the  $E_c - 0.10 \text{ eV}$  configuration under reverse bias was measured by Jellison to be equal to the  $E_c - 0.17 \text{ eV}$  emission time constant. This assures therefore that, in a normal DLTS experiment, all of the defects will have returned to the  $E_c - 0.10 \text{ eV}$  configuration before the next trap filling pulse.) We have used this second simpler technique to separate the two components and obtained the results plotted in Fig. 1, and tabulated in Table I.

The  $E_c - 0.17 \text{ eV}$  peak disappears upon higher temperature annealing in two distinct stages as observed earlier by Jellison.<sup>3</sup> In our samples, the bistable component disappears at  $\sim 300^\circ \text{C}$ . The remaining component disappears at  $\sim 400^\circ \text{C}$ , in close correlation with the O-V anneal which we observe by EPR. In samples 2 and 3 with no O-V centers, the anneal is complete in the first stage.

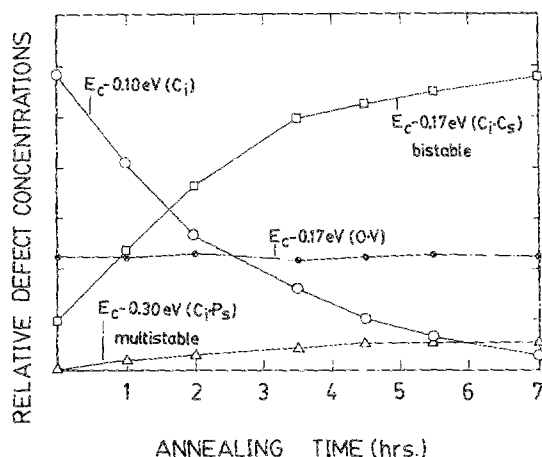


FIG. 1. Defect concentration during isothermal annealing at 303 K for sample 1 following room-temperature irradiation (dose:  $2 \times 10^{15} \text{ e}^-/\text{cm}^2$ ).

From these results, we can conclude the following: The O-V pair gives rise to a normal (not bistable) level at  $E_c - 0.17 \text{ eV}$ . The bistable component at  $E_c - 0.17 \text{ eV}$  emerges only when the  $E_c - 0.10 \text{ eV}$  precursor disappears upon annealing at  $\sim 300\text{--}350 \text{ K}$ . Neither the precursor nor the  $E_c - 0.17 \text{ eV}$  bistable defect requires oxygen. The concentrations of both correlate directly with the carbon concentration. The bistable defect is therefore a distinct carbon-related defect, *unrelated to the O-V pair*.

There is therefore no longer any evidence that the  $E_c - 0.10 \text{ eV}$  precursor is vacancy related as we have previously suggested.<sup>6</sup> Instead we return to the original suggestion by Kimerling *et al.* that it is the *single acceptor level* ( $-/o$ ) of *isolated interstitial carbon* ( $C_i$ ).<sup>9</sup> These workers demonstrated a close correlation of its  $300\text{--}350 \text{ K}$  annealing kinetics to that determined for isolated  $C_i$  by EPR studies.<sup>10</sup> The direct correlation of its concentration with carbon content shown in Table I serves as strong additional confirmation of this identification.

From previous EPR studies in *p*-type material, it has been shown that  $C_i$  are formed as mobile interstitial silicon atoms, produced in the electron damage event, are trapped by substitutional carbon atoms.<sup>10</sup> At  $\sim 300\text{--}350 \text{ K}$  these in turn diffuse through the lattice to be trapped by other de-

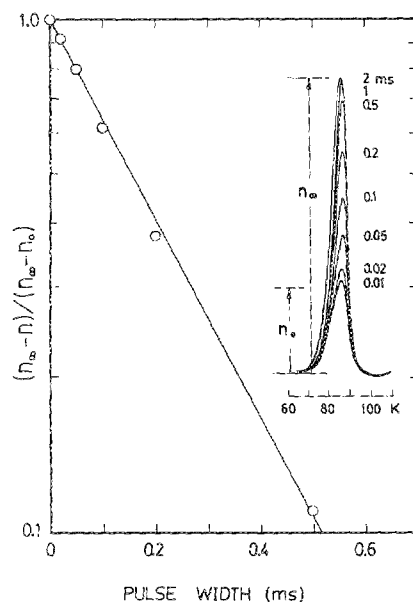


FIG. 2. Amplitude of the  $E_c - 0.17 \text{ eV}$  peak vs pulse width. The rate window was set at  $45.2 \text{ s}^{-1}$  and the time between pulses was  $\geq 75 \text{ ms}$ .

fects. A dominant trap in high carbon content material is a second substitutional carbon atom, and  $C_i-C_s$  pairs are formed, as again identified directly by EPR.<sup>11</sup>

The emergence of the bistable  $E_c - 0.17$  eV level is accompanied by the simultaneous emergence of the four-level multistable defect at  $E_c - 0.30$  eV. We identify these therefore as two distinct carbon-trapped configurations. The 300 °C annealing result for the  $E_c - 0.17$  eV bistable defect closely matches that for the  $C_i-C_s$  pairs in EPR studies.<sup>11</sup> This plus the dependence on carbon concentration, as shown in Table I, leads us to identify the bistable  $E_c - 0.17$  eV defect as arising from a *single acceptor level* (  $- / o$  ) of the  $C_i-C_s$  pair. [The pair has a single donor level (  $o / +$  ) at  $E_c + 0.33$  eV.<sup>2</sup>]

EPR centers have very recently been detected for the  $E_c - 0.10$  eV precursor and for each of the two bistable configurations of the  $E_c - 0.17$  eV defect.<sup>12</sup> In a <sup>13</sup>C-doped sample, we have resolved a weak hyperfine structure from two inequivalent carbon atoms for one of the configurations confirming unambiguously the  $C_i-C_s$  pair identification. These spectra are currently under study and the details will be described in a subsequent publication.

Chantre and Kimerling have previously shown that the concentration of the  $E_c - 0.30$  eV multistable defect depends upon the phosphorus content.<sup>7</sup> Our results in Table I reveal this also, the relative concentrations of the  $E_c - 0.30$  eV level favoring high phosphorus concentration (sample 2 and the sample in Ref. 6), that of the  $E_c - 0.17$  eV bistable defect favoring high carbon concentration (sample 1). We suggest therefore that the four-level multistable defect is a substitutional phosphorus-interstitial carbon pair ( $C_i-P_s$ ). A direct confirmation of this suggestion requires EPR identification, of course, and such experiments are currently being initiated.

A simple scenario therefore appears to be emerging. The primary damage event produces vacancies and silicon interstitials in equal concentrations. The vacancy is mobile below room temperature and the principal trapped vacancy-impurity interactions are well understood.<sup>13</sup> An effective trap for

the interstitials is carbon and the resulting interstitial carbon defect gives rise to a single donor state at  $E_v + 0.27$  eV<sup>2,10,14</sup> and a single acceptor state at  $E_c - 0.10$  eV.  $C_i$  migrates at room temperature to form  $C_i-C_s$  and  $C_i-P_s$  pairs.<sup>15</sup> The proportion of each depends on the relative carbon and phosphorus concentrations. Both of these defects display metastable character, apparently a feature characteristic of the common denominator, the interstitial carbon atom. We are optimistic that a detailed atomic-level view of the mechanism for this carbon-induced metastability may emerge from a complete analysis of the newly observed EPR centers and a study of their interconversions.

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<sup>3</sup>G. E. Jellison, Jr., J. Appl. Phys. **53**, 5715 (1982).

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<sup>5</sup>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.

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<sup>7</sup>A. Chantre and L. C. Kimerling, Appl. Phys. Lett. **48**, 1000 (1986).

<sup>8</sup>In Ref. 6, we report this level as  $E_c - 0.44$  eV, uncorrected for the temperature dependence of capture cross section. Chantre and Kimerling (Ref. 7) have subsequently determined the correction giving the new value  $E_c - 0.30$  eV. We use this corrected value here.

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<sup>11</sup>K. L. Brower, Phys. Rev. B **9**, 2607 (1974).

<sup>12</sup>L. W. Song and G. D. Watkins, B. Am. Phys. Soc. **32**, 403 (1987).

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<sup>14</sup>P. M. Mooney, L. J. Cheng, M. Suli, J. D. Gerson, and J. W. Corbett, Phys. Rev. B **15**, 3836 (1977).

<sup>15</sup>In pulled silicon (high oxygen content), the major DLTS peak produced when interstitial carbon anneals is at  $E_v + 0.38$  eV. It has recently been shown by EPR studies that this defect is interstitial carbon (trapped by interstitial oxygen) [J. M. Trombetta and G. D. Watkins, Appl. Phys. Lett. **51**, 1103 (1987)].