Bistable Defect in Silicon: The Interstitial-Carbon–Substitutional-Carbon Pair

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By combining several spectroscopic techniques, we have observed a new type of bistable center in electron-irradiated silicon and have identified it as an interstitial-carbon–substitutional-carbon pair. The positive and negative charge states of the defect share a common stable configuration which differs from that for the neutral state by a simple molecular bond rearrangement. Detailed structural models and configurational-coordinate energy surfaces are presented for each of the three charge states.

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Defects in solids which display bistable electronic properties are of great current interest. Examples include the *DX* centers in AlGaAs and GaAsP,[1] *EL*2 in GaAs,[2] In in $\mathrm{CdF_2}$,[3] and certain radiation-produced and Fe-related defects in InP[4,5] and silicon.[6-12] Bistability can occur whenever the stable configuration of a defect changes with its charge state and a substantial barrier exists for conversion from one configuration to the other. In the particular case of Fe-acceptor pairs in silicon, a model has been proposed in which the change in Coulomb interaction between Fe^{++} or Fe^{+} interstitial and the negative substitutional acceptor causes a change in the relative stability of the nearest- or next-nearest–neighbor position for the interstitial Fe.[12,13] In no other case, however, is there a well-established picture of the mechanism nor in most cases even of the identity of the defect involved.

In the present Letter, we identify an important new bistable defect in crystalline silicon, an interstitial-carbon–substitutional-carbon pair $(\mathrm{C}_i\mathrm{C}_s)$. We combine results from deep-level transient capacitance spectroscopy (DLTS), electron paramagnetic resonance (EPR), photoluminescence, and optical detection of magnetic resonance (ODMR) to characterize its electronic properties and to provide a detailed microscopic model of its two configurations. To facilitate the presentation, we present at the outset a summary of our final conclusions in Fig. 1. There are two stable configurations—*A* for $(\mathrm{C}_i\mathrm{C}_s)^+$ and $(\mathrm{C}_i\mathrm{C}_s)^-$, and *B* for $(\mathrm{C}_i\mathrm{C}_s)^0$—which differ only by a simple bond-switching transformation. The physical mechanism is therefore qualitatively different from that of the Fe-acceptor pairs and, as such, may provide important new insight into the origin of bistability in other defect systems.

In what follows, we first review the relevant previous work and then outline the step-by-step experiments by which we have established this identification and have determined the energies for the configurational-coordinate surfaces shown in the figure.

Substitutional carbon is a common impurity in silicon. Previous EPR studies in electron-irradiated *p*-type material have established that interstitial $\mathrm{C}_i^{\,+}$ is formed by the capture of mobile interstitial-silicon atoms produced in the displacement-damage event.[14] The interstitial carbon atoms, in turn, are mobile at room temperature and over a period of a few days migrate and are trapped by remaining substitutional carbon atoms to form $(\mathrm{C}_i\mathrm{C}_s)^+$ pairs, again identified by EPR.[15] No evidence of bistability was reported in these studies.

In *n*-type irradiated silicon, on the other hand, a defect with bistable electrical properties has been reported in

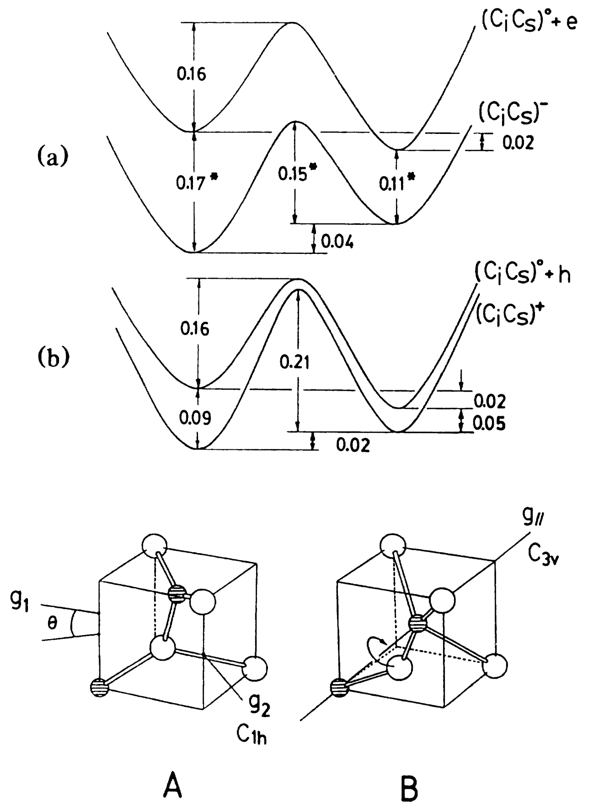

FIG. 1. Models and configurational-coordinate energy curves for the two configurations of the $\mathrm{C}_i\mathrm{C}_s$ pair (units in electronvolts). (a) Acceptor state [the asterisked values determined by Jellison (Ref. 6)]. (b) Donor state. In the models, the smaller, cross-hatched atoms are carbon.

DLTS studies by several workers.[6,7,12] Its properties can be summarized by the asterisked values given on the configurational-coordinate diagram in Fig. 1(a). It has two stable configurations: A when negatively charged, B when neutral. In the A^- state, the electron emission rate indicated a level at $E_c - 0.17$ eV. In the metastable B^- configuration, the level was measured to be at $E_c - 0.11$ eV. The barrier for the conversion $B^- \rightarrow A^-$ was determined to be $\simeq 0.15$ eV.[6] The thermally activated $A^- \rightarrow B^0$ conversion rate was found to be identical to the A^- emission rate,[6] which provides no information therefore about the barrier for the conversion $A^0 \rightarrow B^0$, except that it is < 0.17 eV.

In two recent publications,[16,17] it was proposed that this bistable defect arises from a negative charge state of the C_iC_s pair. The work described in this Letter was initiated to test this suggestion.

First, we report the identification of an EPR signal arising from $(C_iC_s)^-$, proving that an acceptor state does indeed exist in the gap. Shown in Fig. 2(a), it is a spectrum of C_{1h} symmetry previously reported, but not identified, in electron-irradiated n-type material[18] and labeled $G17$. Its spin-Hamiltonian parameters are given in Table I. The arguments for this identification are as follows: (1) It grows in in 1:1 correspondence with the disappearance of an EPR center recently identified with isolated C_i^-.[19] (2) Its intensity correlates directly with the carbon content from sample to sample. (3) Under applied uniaxial stress, alignment of the defect is observed to be similar in magnitude and in reorientation kinetics to that observed in the previous $(C_iC_s)^+$ EPR studies,[15] demonstrating the similar core structures for the two. (4) In an enriched ^{13}C (60%)-^{12}C (40%) sample, additional structure is observed [Fig. 2(b)], which confirms the incorporation of carbon in the defect. Although the structure is not well resolved, a computer simulation assuming hyperfine interaction with two inequivalent C atoms, Fig. 2(c), matches the spectrum very well.

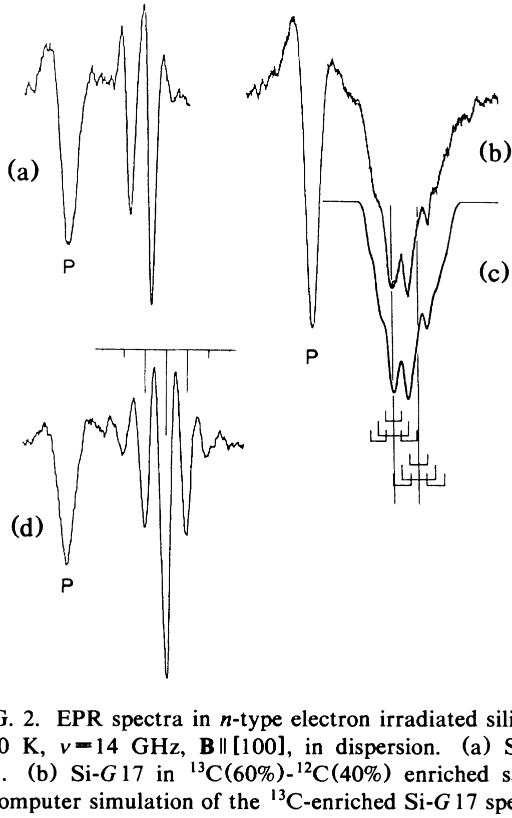

FIG. 2. EPR spectra in n-type electron irradiated silicon at $T \simeq 30$ K, $\nu = 14$ GHz, $\mathbf{B} \parallel [100]$, in dispersion. (a) Si-$G17$ (A^-). (b) Si-$G17$ in ^{13}C(60%)-^{12}C(40%) enriched sample. (c) Computer simulation of the ^{13}C-enriched Si-$G17$ spectrum for two inequivalent C atoms. (d) Si-$L7$ (B^-), showing the satellite structure expected for ^{29}Si hyperfine interaction with 24 equivalent sites.

Next, we demonstrate that the $G17$ EPR center arises from the A^- configuration of the bistable defect seen in the DLTS studies. Upon illumination of the sample at $T < 50$ K with 1.16-eV light from a Nd-doped yttrium aluminum garnet (Nd:YAlG) laser, the $G17$ $(C_iC_s)^-$ spectrum disappears and a new center of C_{3v} symmetry, labeled $L7$, grows in. Shown in Fig. 2(d), a single line is observed for $\mathbf{B} \parallel [100]$ but with rich satellite structure. The spin-Hamiltonian parameters for the spectrum are given in Table I. This new center can be converted back to $G17$ by heating in the dark, the kinetics of which are identical to that for the conversion $B^- \rightarrow A^-$ observed in the DLTS studies.

We conclude therefore that we are observing by EPR both the stable A^- ($G17$) and the metastable B^- ($L7$) configurations of the bistable center observed in DLTS, and that they arise from two different configurations of the $(C_iC_s)^-$ pair. The close similarity of the core structure of the A^- ($G17$) center and the previously studied $(C_iC_s)^+$ center (deduced from the EPR C_{1h} symmetry and the stress alignment studies) suggests that the stable configuration for $(C_iC_s)^+$ is also the A configuration, as illustrated in Fig. 1(b).

This implies, in turn, that bistability should also occur in the p-type studies as the defect cycles between $(C_iC_s)^+$ and $(C_iC_s)^0$. To check this, we have investigated first the behavior of the $(C_iC_s)^+$ EPR signal in p-type material under Nd:YAlG injection. We find indeed that the $(C_iC_s)^+$ signal disappears, consistent with a conversion to the B state. No new EPR signal is observed. Thermally activated recovery of the $(C_iC_s)^+$

TABLE I. Spin-Hamiltonian parameters for Si-$G17$ and Si-$L7$ (the defect axes are shown in Fig. 1).

Si-$G17$ (A^-) (C_{1h})	Si-$L7$ (B^-) (C_{3v}, $T > 15$ K)
$g_1 = 2.0001$	$g_\parallel = 2.0008$
$g_2 = 2.0021$	$g_\perp = 1.9994$
$g_3 = 2.0027$	
$\theta = 16°$	

signal reveals an activation barrier of 0.21 eV, which has been included in Fig. 1(b) for the conversion $B^+ \rightarrow A^+$.

Previous ODMR studies have demonstrated that a prominent luminescence band in electron-irradiated silicon with zero-phonon line at 0.97 eV also arises from a center involving two carbon atoms.[20] From the close similarity of production and annealing temperatures to that for the $(C_iC_s)^+$ pair in EPR studies, it was concluded that it also arises from the C_iC_s defect.

We have therefore reinvestigated the 0.97-eV luminescence to check for evidence of this bistability. Using the Nd:YAlG laser for excitation we find the identical bistable features in the luminescence: (1) In high-resistivity material, where the stable state is B^0, the luminescence is present initially with no change in intensity with time. (2) In low-resistivity *n*-type or *p*-type material, where A is the stable configuration, the 0.97-eV luminescence is initially not present (*n* type), or weak (*p* type), but grows in with time in direct quantitative correlation to the $A \rightarrow B$ conversion observed by EPR in each of these materials. (3) The thermal recovery back to the A configuration as monitored in the photoluminescence studies matches accurately the two distinct thermally activated processes found from the EPR studies in each of the *n*- and *p*-type materials.

We have therefore confirmed directly that the 0.97-eV luminescence arises from the same C_iC_s bistable center, and we have obtained the important new information that it arises from the *B configuration* only.[21] This is also confirmed by the close similarity of the B^- ($L7$) EPR spectrum and the ODMR spectrum of the luminescence.[20] Both display lower symmetry at very low temperatures but motionally average to C_{3v} at $T \simeq 15-30$ K. In the motionally averaged state, both display the curious satellite structure shown in Fig. 2(d). As pointed out in the ODMR studies,[20] this structure could be explained as arising from hyperfine interaction with ^{29}Si ($I=\frac{1}{2}$, 4.7% abundant) if the wave function for the spin in the motionally averaged state were spread equally over $\simeq 24$ Si neighboring atom sites. From the ODMR studies, additional ^{13}C hyperfine interactions with two equivalent carbons and one single Si atom led to a model of two substitutional carbon atoms with the silicon atom squeezed between in a position away from the bond center. This is illustrated in Fig. 1, which we can now assign to the B configuration. This model is fully consistent with the B^- ($L7$) EPR signal if we assume that the paramagnetic electron state is spread over a cage of $\simeq 24$ silicon atoms, and if for the excited $S=1$ B^0 state involved in the luminescence the accompanying hole is localized primarily on the C_s-Si-C_s core.

Finally, we have also confirmed bistable electrical properties for the defect by DLTS in *p*-type material. We find emission from the $A^{(0/+)}$ donor state characteristic of a level at $E_v + 0.09$ eV,[22] as indicated in Fig. 1(b). We find no evidence in these studies of a deep donor state for the B configuration. The full bistable intraconversion between A and B has been confirmed for this level. In addition, the $A^0 \rightarrow B^0$ kinetics can now be measured for the first time giving a barrier of 0.16 eV, which has also been included in Figs. 1(a) and 1(b).

In Fig. 1, we summarize therefore what we have learned about the configurational energy surfaces for the three charge states of the C_iC_s defect. In the figure we have included also (1) the difference in energy between the A^0 and B^0 minima [determined from the amplitude of the A^+ DLTS emission peak after equilibration between the configurations in the neutral state (reverse bias)], and (2) the location of the B^+ minimum [determined from the equilibrium B concentration versus Fermi level as monitored by the initial luminescence in *p*-type material of different acceptor dopants (B, Al, Ga)]. We note that we have been able to determine all of the relevant energies and barriers for each of the three charge states of the defect. We believe that this is the first bistable defect in any solid for which such detailed information has been obtained.

At the same time, we have identified the defect and can propose detailed microscopic models for each configuration, as shown in Fig. 1. We have already described the B configuration as deduced from the ODMR studies. In the A configuration our model has one substitutional carbon atom next to a carbon "interstitialcy" in which a carbon-silicon "molecule" shares a single lattice site, each component being threefold coordinated. This is fully consistent with the EPR results for the A^+ and A^- configurations and also with that for the isolated carbon interstitial which displays this ⟨100⟩ oriented "interstitialcy" character.[14]

The bistability comes therefore from a molecular rebonding presumably driven by the energetically unfavorable A^0 state which must accommodate two electrons into nonbonding orbitals on the threefold-coordinated atoms. It is interesting to note that the reorientation kinetics observed by EPR for A^+ and A^- indicate a barrier of $\simeq 0.2$ eV,[15] close to that for the $B \leftrightarrows A$ barrier deduced from the bistable behavior. This suggests that reorientation goes by way of bond switching to the B configuration, which is symmetrically disposed with respect to the three possible orientations of the Si-C interstitialcy.

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[21] This result was recently anticipated by Asom *et al.* (Ref. 16) from the observation that injection conditions similar to that under photoluminescence excitation effectively converts $A \rightarrow B$. This interpretation appeared in conflict, however, with evidence from resolved carbon local-mode structure on the 0.97-eV band [G. Davis, E. C. Lightowlers, and M. do Carmo, J. Phys. C **16**, 5503 (1983)] which had been interpreted to indicate instead configuration A, with B also involved (Ref. 20), but only indirectly in the luminescence pumping cycle. Our present results confirm the suggestion of Asom *et al.*, forcing a new interpretation of the local-mode structure which we will describe in a forthcoming publication.

[22] A level at $E_V + 0.33$ eV has been attributed to the donor state of the C_iC_s pair by L. C. Kimerling, in *Radiation Effects in Semiconductors—1976,* edited by N. B. Urli and J. W. Corbett, IOP Conference Proceedings No. 31 (Institute of Physics, London, 1977), p. 221. This apparently was an error. We detect no such level in our studies.