EPR Observation of the Isolated Interstitial Carbon Atom in Silicon*

G. D. Watkins

Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015

and

K. L. Brower

Sandia Laboratories, Albuquerque, New Mexico 87115 (Received 12 April 1976)

An EPR spectrum, labeled Si-G12, is identified as arising from an isolated interstitial carbon atom in silicon. A $\langle 100 \rangle$ C-Si interstitialcy model is suggested for the defect in which a silicon and carbon atom pair partially share a single substitutional site. Because carbon is isoelectronic with silicon, these results suggest a similar $\langle 100 \rangle$ Si-Si interstitialcy configuration for the silicon self-interstitial, a fundamental defect which has so far eluded direct detection.

In this Letter, we report the observation by EPR of a defect which we identify as the isolated interstitial carbon atom in silicon. It is found to be one of the dominant EPR centers produced in some ingots of commercially available "high purity" *p*-type floating-zone-refined silicon when irradiated by 1.5-MeV electrons in the temperature range 100-300 K. We thus supply direct confirmation of the important role played by trace amounts of carbon in the radiation-damage behavior of silicon. In addition, this observation is of particular importance because interstitial carbon, being isoelectronic to silicon, provides important clues as to the configuration and properties of the isolated interstitial silicon atom (self-interstitial), which so far has eluded detection.

The EPR spectrum that we identify with isolated interstitial carbon was first reported in 1964 and labeled Si-G12.¹ At that time it could not be identified and no model for the defect was proposed. It has orthorhombic symmetry with $g_1[110] = 2.0020$, $g_2[\overline{110}] = 2.0062$, and $g_3[001]$ = 2.0068, indicating a defect with C_{2v} symmetry and spin $S = \frac{1}{2}$.

In this Letter, we extend the study to vacuum-floating-zone-refined *p*-type silicon $(B \sim 10^{15}/\text{cm}^3)$ which has been specially doped with carbon $(\sim 10^{17}/\text{cm}^3)$ enriched to 60.1% ¹³C, 39.9% ¹²C. The Si-G12 spectrum produced by irradiation of this sample is shown in Fig. 1. Hyperfine satellites reflecting the ¹³C (nuclear spin $I = \frac{1}{2}$) isotopic abundance reveal unambiguously that a single carbon atom is incorporated in the defect. The ¹³C hyperfine tensor components are $|A_1[110]| = 6.24$, $|A_2[\overline{110}]| = 48.60$, and $|A_3[001]| = 5.87$ in units of 10^{-4} cm⁻¹. Using the values $|\psi_{2s}(0)|^2 = 18.8 \times 10^{24}$ cm⁻³ and $\langle r_{2p}^{-3} \rangle = 11.6 \times 10^{24}$ cm⁻³, previously es-

timated for neutral carbon,² these hyperfine components indicate that 36% of the unpaired spin wave function is located on the carbon atom, which has 97% 2p and 3% 2s character. In Fig. 1, resolved ²⁹Si hyperfine interactions can also be seen whose total intensity corresponds to ~ 6-8 neighboring sites. A substantial part of the remaining portion of the wave function is localized on these silicon atoms.

Further confirmation of the identification comes from annealing studies. The Si-G12 spectrum is observed to disappear in a 30-min isochronal annealing sequence at ~65°C. Coincident with its disappearance, another spectrum, labeled Si-G11,



FIG. 1. Si-G12 spectrum at $\nu = 19.8582$ Hz, $\vec{H} || \langle 100 \rangle$, T = 35 K. Hyperfine satellites due to ¹³C (enriched to 60.1%) and ²³Si (normal abundance 4.7%) are indicated.

emerges. The Si-G11 spectrum has previously been identified as a Jahn-Teller-distorted $\langle 111 \rangle$ C-C interstitialcy²; this study was performed on samples from the same enriched ¹³C silicon boule. The annealing process can therefore be identified as diffusional migration of the interstitial carbon atom at this temperature and subsequent trapping by substitutional carbon to form the pairs.

(The Si-G11 spectrum was also first reported¹ in 1964. In that report, it was stated that the Si-G11 spectrum was observed after irradiation at 100 K. That statement was apparently in error. We have not been able to reproduce those results nor has it been possible to locate any evidence in the original data to support the statement. The Si-G11 spectrum appears to be produced by irradiation only at or above room temperature, consistent with its formation requiring interstitial carbon migration.)

A model for the Si-G12 center which is consistent with the observed C_{2v} symmetry and ¹³C hyperfine interactions is shown in Fig. 2. This configuration corresponds to a $\langle 100 \rangle$ Si-C interstitialcy. Such a configuration was originally proposed by Friedel³ for interstitial silicon. This is



FIG. 2. A model for the Si-G12 center, showing the principal axes for the defect. A $\langle 100 \rangle$ C-Si interstitialcy is illustrated where the C-Si dumbell occupies a single substitutional site. The C_{2v} symmetry is also satisfied if the carbon atom lies anywhere along the line between the interstitial tetrahedral site (T_d) and the substitutional site (dot).

also one of two interstitialcy configurations that appear to be strongly favored in molecular-orbital cluster calculations for the diamond lattice.⁴⁻⁶ (The other favored configuration corresponds to a $\langle 111 \rangle$ interstitialcy and is inconsistent with the C_{2v} symmetry observed for the Si-G12 spectrum.) The EPR state has a single positive charge, the unpaired electron residing primarily in the lonepair nonbonding p orbital on the carbon atom as shown. The corresponding orbital on the silicon atom is perpendicular to that and empty. The fact that the carbon orbital is occupied rather than the silicon orbital is consistent with the fact that carbon has a larger electronegativity than silicon. These orbital configurations are also similar to those found from the cluster calculations for interstitial nitrogen⁶ in this molecular configuration in diamond.

Actually, our EPR measurements indicate only that the carbon atom resides somewhere between a normal tetrahedral interstitial site and the normal substitutional site, the locus of all possible positions satisfying $C_{2\nu}$ symmetry. In the arguments to follow we will derive some insight as to how much the carbon atom may be displaced toward the substitutional site, but the details concerning this model will probably only emerge from a detailed study such as electron-nuclear double resonance for the silicon neighbors.

Application of uniaxial stress along a $\langle 110 \rangle$ direction at $T \sim 270$ K produces a preferential alignment of the Si-G12 centers which can be studied by cooling to the EPR observation temperature (20-35 K) with stress on, removing the stress, and monitoring the relative EPR intensities. Writing the energy of the defect in an applied strain, ϵ_{ii} , as

$E = \sum B_{ij} \epsilon_{ij},$

preliminary analysis of the observed alignment gives for the traceless components of the elastic coupling tensor $B_{11} \simeq +7.3$ eV, $B_{22} \simeq +0.3$ eV, and $B_{33} \simeq -7.6$ eV. All other components are zero by symmetry. The axes are the 1, 2, 3 principal axes of the defect as shown in Fig. 2. These are sizable coupling coefficients and may be interpreted as reflecting substantial bonding character for the carbon atom. The value of $B_{33} = -7.6$ eV reflects the incompressibility of the defect along its 3 axis. This result is intuitively reasonable because two atoms are crowded into one space along this direction (Fig. 2). The higher positive value for B_{11} than for B_{22} indicates that the defect prefers to align itself with its 1 axis



FIG. 3. Characteristic reorientation time τ for the Si-G12 center versus temperature.

along the compressed direction, another measure of the substantial difference between the bonding character at the carbon and silicon halves of the interstitialcy. The fact that the 1 axis rather than the 2 axis of the defect tends to align itself along the compressed direction is consistent with the smaller size of the carbon atom.

Recovery from the alignment was studied by a series of isothermal anneals. The results are shown in Fig. 3. The activation energy required for the reorientation process was determined to be 0.88 ± 0.03 eV. The large activation energy again may be interpreted as evidence for a substantial displacement into the "bonding" interstitialcy position. Attempts were made to enhance the reorientation by light at 15, 100, and 150 K, but no effect was observed.

At 65°C, the Si-G12 spectrum converts to the Si-G11 spectrum with a time constant of ~ 30 min. During this time, the kinetics of Fig. 3 predict ~10⁶ reorientational jumps. This is roughly the number of diffusional jumps that an interstitial carbon must make in order to encounter a substitutional carbon atom (concentration ~ 10⁻⁶), which suggests that the reorientation jump process may also involve migration of the defect. Long-range migration would not be possible if reorientation occurred simply by tumbling of the C-Si dumbbell at a given substitutional site, or as reorientation of a $\langle 100 \rangle$ Jahn-Teller distortion around a single tetrahedral interstitial site. Long-range migration could occur, however, if reorientation occurs by interstitialcy migration where the carbon atom moves to share the site of its neighbor.

Stein and Vook^{7,8} showed that irradiation-produced infrared absorption bands at 922 and 932 cm⁻¹, previously observed by Whan⁹ and Whan and Vook,¹⁰ are carbon-associated centers. Bean and Newman¹¹⁻¹³ have identified these absorption bands in terms of a single interstitial carbon atom. Consistent with our results, these bands disappear upon annealing^{10, 12, 14} in the same temperature range as we observe for the Si-G12 spectrum. There are differences, however. Bean and Newman have concluded that the defect has C_{3v} symmetry in order to explain the two bands of $\sim 1:2$ intensity. The symmetry of the defect in Fig. 2 is such as to allow for three separate modes. The infrared bands, seen mainly in ntype and high-resistivity silicon, probably refer to the neutral charge state, while the EPR spectrum seen in p-type material is for the positively charged state. The two sets of results could possibly be reconciled therefore if the configuration of the defect changes with charge state. Our failure to enhance reorientation by light, however, does not confirm this. It may be that only two bands of intensity 2 and 1 are observed due to accidental degeneracy. In this respect, it is important to realize that the elastic coupling tensor which we have determined is associated with the whole defect whereas the *localized* vibrational modes associated with the carbon atom reflect primarily the bonding of the carbon, not the carbon-silicon pair, to the surrounding lattice. Further studies are required before these differences are understood.

In summary, we identify one of the dominant stable defects produced by irradiation of highpurity silicon as the isolated interstitial carbon atom. It is presumably formed when a mobile self-interstitial, produced in the primary event. is trapped by a substitutional carbon-atom impurity. (The high mobility of the self-interstitial in silicon at cryogenic temperatures has been previously established by EPR studies in aluminum¹- and boron¹⁵-doped silicon.) The results of our EPR measurements suggest that the configuration of the defect corresponds to a (100) Si-C interstitialcy. Since carbon is isoelectronic with silicon, these results suggest further that a possible configuration for the silicon self-interstitial is a $\langle 100 \rangle$ Si-Si dumbbell centered on a substitutional site.

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Diffuse-Neutron-Scattering Measurements of the Fractional Occupancy of the Localized $4f^1$ Configuration in Ce-Th and CeAl₃ †*

A. S. Edelstein

University of Illinois, Chicago, Illinois 60680, and Argonne National Laboratory, Argonne, Illinois 60439

and

H. R. Child

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

and

C. Tranchita University of Illinois, Chicago, Illinois 60680 (Received 19 January 1976)

Diffuse-neutron-scattering measurements at $2 \le T \le 300$ K have been employed to determine the fractional occupancy η of the localized $4f^1$ configuration. For CeAl₃, $\eta = 0.9 - 1.0$ at 11 K. For Ce_{0.8}Th_{0.2}, $\eta = 0.4 \pm 0.1$ at 11 K. No evidence of a compensating conduction-electron polatization was observed.

The collapsed phase of some systems, e.g., SmS under pressure, $Sm_{1-x}M_xS$ (M = Gd, Y, La), and $SmAs_xS_{1-x}$, are believed to be configurationfluctuation (CF) systems. These are systems which exist an appreciable fraction of time in more than one electronic configuration; e.g., in SmS under pressure, both the $4f^5$ and $4f^6$ configurations are occupied. X-ray photoemission measurements¹ have determined the fractional occupancy of these two configurations in anion-substituted SmS. Inelastic-neutron-scattering measurements² have established an upper bound of 10%on the amount of valence mixing in the black phase of SmS. It has been suggested that CeAl, α -Ce, and the α phase of CeTh alloys may be CF systems. Here we present evidence based upon diffuse-neutron-scattering measurements which

show that the α phase of Ce_{1-x} Th_x alloys (x=0.2, 0.266, 0.29) and possibly CeAl₃ are CF systems. No evidence of a compensating conduction-elec-tron polarization was observed in either system.

The square of the effective moment $\mu_{eff}^2 = 3kT\chi/A$ of Ce can be reduced by (1) crystal fields, (2) a small value for the spin correlation time τ , (3) a compensating conduction-electron polarization, and (4) a small value for the fractional occupancy of the localized $4f^1$ configuration, η . Using the fluctuation-dissipation theorem and the Kramers-Kronig relations, one can show that susceptibility measurements average $\langle J(0) J(t) \rangle$ over a time proportional to T^{-1} . The susceptibility at low temperatures is determined by both η and τ . In contrast, diffuse-neutron-scattering measurements with sufficiently energetic neutrons deter-