Identification of an interstitial carbon-interstitial oxygen complex in silicon

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An electron paramagnetic resonance spectrum, observed in electron irradiated silicon and labeled *Si-G15*, is shown to originate from the same carbon-oxygen complex as does the well studied C-line photoluminescence spectrum with zero-phonon line at 0.79 eV. Both the g tensor and the ^{13}C hyperfine tensor for this center are remarkably similar to those for the isolated interstitial carbon atom. Stress-induced alignment experiments reveal the role of oxygen and indicate a unique structure for an interstitial carbon-interstitial oxygen pair.

Among the dominant spectroscopic features produced by room-temperature electron irradiation of Czochralski silicon are the G15 electron paramagnetic resonance (EPR) center,[1] or the *K* center,[2] and the 0.79-eV C-line photoluminescence (PL) center.[3] In this letter we show that these two spectra arise from the same defect which we identify for the first time as an interstitial carbon-interstitial oxygen $[C_i\text{-}O_i]$ complex.

The EPR spectrum, G15, first reported in 1964,[1] has spin $S = 1/2$ and C_{1h} (monoclinic *I*) symmetry. It is not produced in floating zone refined silicon, demonstrating its dependence upon oxygen for formation.[1] An electrical level at $E_v + 0.38$ eV has been observed by deep level transient spectroscopy (DLTS) in this material and correlated with G15 by Mooney *et al.*[4]

The C-line PL spectrum has been studied extensively.[3,5–12] Stress splitting experiments on the zero-phonon line indicate a center with C_{1h} symmetry and an electric dipole transition moment along the C_{1h} axis.[5] Thonke *et al.*[9] have recently shown that the C line originates from the recombination of a shallow electron and a deep hole which has a binding energy to the defect of 0.34 eV. Observations of shifts of the zero-phonon line energy due to ^{13}C and shifts in two local mode replicas due to [18]O have confirmed the presence of these two atoms in the structure.[7,12] Recently, a close correlation was demonstrated between the C line and an infrared local mode absorption band labeled C(3),[8] which had been ascribed to a $[C_i\text{-}O_i]$ pair.[13] Both the G15 and the C line are produced by a 300-K anneal of low-temperature irradiated Czochralski silicon and anneal out at 350–450 °C.[11,14]

Other workers have suggested a correlation between the G15 center and the C-line center[6] and also between the G15 center and the C(3) center.[15] However, Lee *et al.*[15] concluded from an EPR study that the G15 center is a carbon-oxygen-*divacancy* complex with dangling silicon bond character. This model conflicts with the assignment of the C(3) band to a $[C_i\text{-}O_i]$ pair,[13] and thus the validity of these correlations has been in doubt.

In their EPR work, Lee *et al.*[15] demonstrated that the G15 centers can be aligned by applying uniaxial stress at elevated temperatures. In our present work we utilize stress-induced alignment as measured in both EPR and PL to provide, for the first time, an unambiguous demonstration that the C line and the G15 do indeed arise from the same defect. We then extend the studies on the EPR spectrum using un-

iaxial stress and ^{13}C doping to deduce a detailed structural model.

The energy of a defect in an applied strain, ϵ_{ij}, can be written as

$$E = \sum B_{ij}\epsilon_{ij} , \tag{1}$$

where the B_{ij} is an element of the "piezospectroscopic" tensor defined in the defect axis system (Fig. 1).[16] At a sufficiently high temperature, the defects will be free to reorient and, thus, an applied uniaxial stress will produce a preferential alignment.

For a [100] stress there are only two inequivalent sets of orientations for a C_{1h} center, differing by the direction of the defect z axis (Fig. 1) with respect to the [100] stress direction. In EPR the relative populations in different orientations can be determined directly from the relative intensities of the corresponding lines. For the C line we measure the emitted light intensity polarized along [100], I_{100}, and that polarized along [010], I_{010}. For a defect with a transition dipole moment along the C_{1h} axis,[5]

$$\frac{p_\perp}{p_\parallel} = \frac{2I_{100}}{2I_{010} - I_{100}} , \tag{2}$$

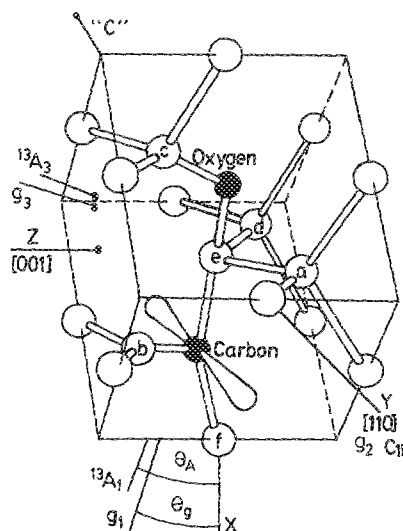where $p_\parallel$ and $p_\perp$ are the fractions of the defects with z axes

FIG. 1. Model for the *Si-G15* center, showing the defect axis systems. Both the oxygen and the carbon lie in the $Y = 0$ plane.

parallel to and perpendicular to the stress, respectively.

The samples were subjected to a 320-MPa compressional stress along [100] at 300 °C for 30 min. The resulting alignment was "frozen-in" by cooling with the stress on and then measured as described. Assuming an equilibrium Boltzmann distribution among the various orientations at 280 °C, we calculate the B_{zz} component of the *traceless* elastic coupling tensor. The resulting values, $B_{zz} = -8.4$ eV for G15 and $B_{zz} = -8.1$ eV for the C line, are in excellent agreement.

The samples were then heated isothermally at 229 °C. The alignment $(p_\perp - p_{10})$ was observed to decay exponentially from its initial value, $(p_\perp - p_{10})_i$, as seen in Fig. 2. Here, p_{10} is the equilibrium value of 2/3. Both the C line and the G15 data agree with a time constant of $\tau = 4.0 \times 10^3$ s. This clearly demonstrates that the two spectra arise from the same defect.

The G15 spectrum was also studied in a crystal of floating zone refined p-type silicon (10^{15}/cm^3 boron) doped with carbon (10^{17}/cm^3) enriched to 60% ^{13}C, 40% ^{12}C. Oxygen was first introduced into the sample by heating in air at 1325 °C for 144 h. The spectrum, as produced by subsequent $1.3 \times 10^{17} e^-$/cm^2 irradiation and observed at 20 K, is shown in Fig. 3. Hyperfine satellites due to ^{13}C (nuclear spin $I = 1/2$), of relative intensity reflecting the ^{13}C abundance, show the presence of a single carbon atom in the defect.

The ^{13}C hyperfine interaction tensor was deduced from the angular dependence of the spectrum. In Table I, we note a remarkable similarity to the hyperfine tensor for the isolated interstitial ^{13}C atom as determined previously[17] from its EPR spectrum, *Si-G12*. In both cases, the unpaired electron resides largely on the carbon atom in a p orbital, oriented along the g_2 axis. The g tensors (Table I) also demonstrate this close resemblance. These results indicate that the carbon atom in the G15 center is interstitial, and is only slightly disturbed from its isolated configuration. We note that, while Lee *et al.*[15] have reported ^{29}Si satellites of G15 split by large hyperfine interactions, these lines do not appear in our spectra. We conclude that the satellites seen by these workers do not belong to the G15 spectrum and that there is
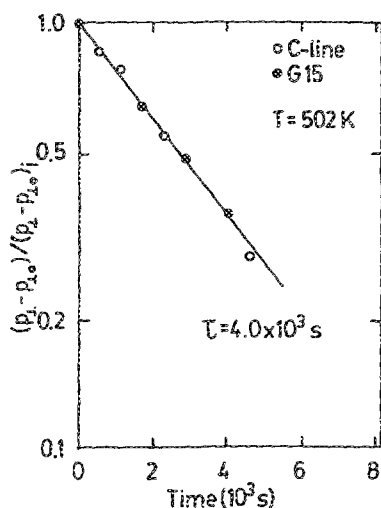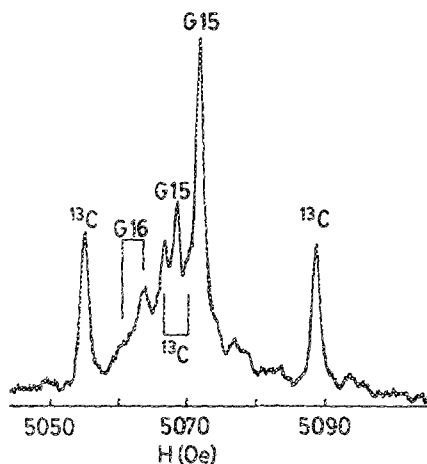

FIG. 3. *Si-G15* spectrum at $v = 14.2210$ GHz, $\mathbf{B} \parallel \langle 100 \rangle$, $T = 20$ K. Hyperfine satellites due to ^{13}C (enriched to 60%) are indicated. A weak *Si-G16* spectrum also appears.

no evidence for dangling silicon bond character.

The structure of the isolated interstitial carbon atom as deduced by Watkins and Brower,[17] involves a $g_3 \langle 100 \rangle$ oriented [C–Si] bonded pair, occupying a single lattice site. In a 270 K stress-alignment study, these workers determined the strain coupling along this g_3 axis, $B_{zz} = -7.6$ eV. The similarity in B_{zz} between G15 and isolated carbon suggests that the $\langle 100 \rangle$ [C–Si] interstitialcy is preserved in the G15 complex.

Another sample was subjected to a stress of 360 MPa along a $\langle 110 \rangle$ direction at 300 °C. Analysis of the resulting alignment indicates that the G15 is not completely free to reorient at this temperature. We describe the defect as having a characteristic $\langle 111 \rangle$ axis, "C", shown in Fig. 1. Under a $\langle 110 \rangle$ stress, the crystal $\langle 111 \rangle$ axes are no longer equivalent. We observe, however, that the set of three orientations with their "C" axes along the same crystal $\langle 111 \rangle$ maintains a fixed population under the stress. This suggests that the G15 complex is an interstitial carbon atom which is perturbed by a second *immobile* defect along this $\langle 111 \rangle$ direction.

In an independent experiment, an "as-grown" sample was subjected to a $\langle 110 \rangle$ stress of 350 MPa at 450 °C in order to align the isolated interstitial oxygen atoms.[18] The sample was then irradiated at room temperature to form G15

FIG. 2. Isothermal recovery of alignment at 229 °C.

TABLE I. Spin Hamiltonian parameters for the *Si-G15* and *Si-G12*; the ^{13}A components are given in units of 10^{-4} cm^{-1}.

Si-G15	*Si-G12*[a]
$^{13}A_1 = 2.0 \pm 1.0$	$^{13}A_1 = 6.24$
$^{13}A_2 = 43.2 \pm 0.5$	$^{13}A_2 = 48.60$
$^{13}A_3 = 3.0 \pm 1.0$	$^{13}A_3 = 5.87$
$\theta_A = 20° \pm 5°$	$\theta_A = 0°$
$g_1{}^b = 1.9998 \pm 0.0003$	$g_1 = 2.0020 \pm 0.0003$
$g_2 = 2.0062 \pm 0.0003$	$g_2 = 2.0062 \pm 0.0003$
$g_3 = 2.0052 \pm 0.0003$	$g_3 = 2.0068 \pm 0.0003$
$\theta_g = 18.5° \pm 1.0°$	$\theta_g = 0°$

[a] Reference 17.
[b] Reference 1.

centers. The resulting G15 population was found to have a ⟨111⟩ alignment of the same sense as is known for the ⟨111⟩ oriented oxygen interstitial.[18] This provides dramatic evidence that the nearby *immobile* defect is an interstitial oxygen, which retains its ⟨111⟩ bond-centered isolated configuration upon pairing with the interstitial carbon atom. The inability to reorient the oxygen at 300 °C is consistent with the tendency for isolated oxygen to remain immobile until roughly 420 °C.[18]

A structural model for the G15 complex which is consistent with the properties of the EPR spectrum and stress alignment results is included in Fig. 1. The general configurations of the isolated carbon and oxygen interstitials are preserved while satisfying the requirement of C_{1h} symmetry. Note that the Si-O-Si "molecule" is oriented along the characteristic ⟨111⟩ axis, "C". The local vibrational modes, known from the C(3) band and the C-line PL sidebands, fall in the frequency range of the two isolated interstitials.[8,10] This structure, therefore, is consistent with the observed modes.

The local strain field of the isolated carbon is known to be tensile along the ⟨110⟩ direction perpendicular to g_2 (Ref. 17) while that of the isolated oxygen is compressive along its ⟨111⟩ axis.[18] In the configuration of Fig. 1, these strain fields tend to cancel. It is evident that this reduction of total anisotropic strain energy plays a role in the mechanism by which the two atoms are bound.

In summary, we have demonstrated that the 0.79-eV C-line optical transition and the G15 EPR spectrum arise from the same defect, which we identify as an interstitial carbon atom which is trapped near an interstitial oxygen atom. The G15 spectrum arises from the singly positive charge state, the hole being located mainly in a nonbonding p orbital of the carbon atom. This structure can, in turn, be identified as

the core of the "pseudodonor" excited neutral state involved in the C-line optical transition. These conclusions apply also to the C(3) infrared band and the $E_v + 0.38$ eV electrical level observed in DLTS since they have both been shown to originate from this center.[8,4]

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