

Interstitial-Carbon Hydrogen Interaction in Silicon

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The T -line luminescence system is created in Si by annealing at 400–600 °C. Shifts and splitting of the spectral features with ^{13}C and D isotope substitution identify the presence of two C atoms and one H atom in the center. Uniaxial stress and magnetic field measurements show that the T center has monoclinic I symmetry and possesses an acceptor ($-/0$) level at 0.2 eV below the conduction band. *Ab initio* cluster calculations lead to a structure in which an interstitial C-H defect binds with a substitutional C atom. The calculated vibrational modes are in good agreement with those observed. [S0031-9007(96)01761-9]

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It is well established now that hydrogen is a common contaminant in silicon [1–4]. It can interact with both shallow and deep level centers and eliminate their electrical [1] and optical [1,4] activity. However, hydrogen can have a quite different effect. In this Letter we report the structure and properties of an optical center created in silicon which is stabilized by the interaction between hydrogen and interstitial carbon. This center gives rise to the T -line (0.9351 eV) luminescence system which is created in either float-zone (FZ) or Czochralski (CZ) grown silicon by radiation damage and subsequent thermal treatment in the temperature range 400–600 °C, or by thermal treatment alone in carbon-rich CZ Si [2–6]. It can also be created in some [5,6], but not all [7], FZ Si by thermal treatment without radiation damage. This center has been long known to be carbon related, a conclusion originally based on sample statistics [5], but subsequently confirmed by a shift in the zero-phonon line with ^{13}C isotope substitution [6]. However, recent investigations of silicon deliberately doped with hydrogen-deuterium mixtures have shown that hydrogen is also involved in this center [2–4]. We present the effects of isotope substitution on the local vibrational mode features observed in the luminescence spectra, the effects of uniaxial stress and magnetic field perturbations on the zero-phonon line, and temperature dependence measurements. These show that the center contains two inequivalent carbon atoms and one hydrogen atom, has monoclinic I symmetry, and creates an electron trap at 0.2 eV below the conduction band. Within these constraints, we use *ab initio* local density functional cluster theory to show that the structure consists of a $\langle 100 \rangle$ oriented pair of carbon atoms which share a lattice site, together with one hydrogen atom attached to one of the carbon atoms. The calculation also allows us to assign

the four observed local vibrational modes and account for their isotope shifts.

The material employed in the work reported here was mainly FZ silicon with $[\text{C}] \sim 2 \times 10^{17} \text{ cm}^{-3}$; one sample had a $^{13}\text{C}/^{12}\text{C}$ ratio of ~ 1.4 . All the material was saturated with $\sim 1.5 \times 10^{16} \text{ cm}^{-3}$ H, D, or a H + D mixture by heating in flowing gas for 30 min at 1300 °C, and rapidly cooling in silicone oil [8]. The material was then irradiated with a flux of either 10^{17} cm^{-2} neutrons, with a Cd ratio of 25, or $2 \times 10^{17} \text{ cm}^{-2}$ 2 MeV electrons, followed by annealing for 30 min at 450 °C. The photoluminescence (PL) was excited by a 514 nm Ar^+ laser and detected with a Fourier transform spectrometer fitted with a North Coast cooled Ge diode detector. Uniaxial stress measurements were made with stresses up to 160 MPa. Magnetic fields up to 5 T were employed.

Figure 1 shows a PL spectrum of the T -line system obtained at 35 K from a sample saturated with deuterium. The line at 1.75 meV higher energy than the T line is associated with a zero-phonon transition from a higher excited state. The phonon-assisted region at lower energy contains a broad sideband of perturbed lattice modes, typical of carbon-containing defects [9], together with several local mode satellites L_3 – L_5 and resonance modes L_1 and L_2 . Above 10 K, all the L mode features are doublets mirroring the two zero-phonon transitions, showing that these features are all associated with the same defect.

We first discuss the isotopic shifts of local mode features which reveal the chemical composition and atomic structure of the center. In $^{12}\text{C} + ^{13}\text{C} + \text{H}$ and $^{12}\text{C} + \text{H} + \text{D}$ mixed isotope materials, the T line splits into two components establishing that the center contains carbon and hydrogen (Fig. 1). Similar isotopic splitting can be observed for the zero-phonon transition associated with the

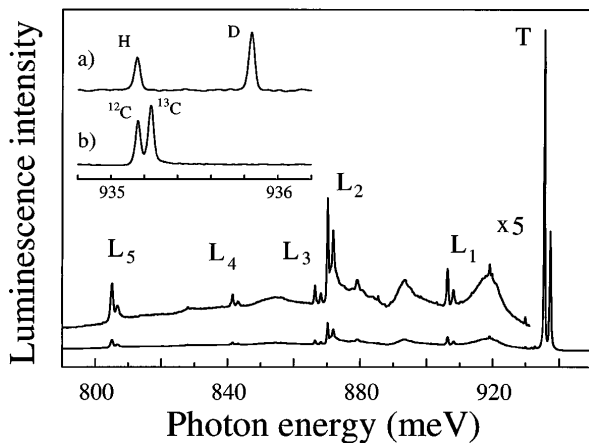


FIG. 1. PL spectrum of the T -line luminescence system recorded at 35 K. The local mode satellites are labeled L_j . The inset shows the isotope splitting of the zero-phonon line at 4.2 K in material containing (a) $^{12}\text{C} + \text{H} + \text{D}$ and (b) $^{12}\text{C} + ^{13}\text{C} + \text{H}$.

higher energy excited state. However, unlike the zero-phonon line, the L_5 local mode splits into four components in the mixed carbon isotope material (Fig. 2) which unambiguously shows that the defect contains two inequivalent carbon atoms, contrary to a previous conclusion [6]. The splitting of a zero-phonon line is dependent on the nature of the electron-phonon coupling [10], and, although this effect is extensively used for chemical characterization, it does not unambiguously reflect the atomic structure of the center. The modes and their isotope shifts are listed in Table I. They give no indication that more than one hydrogen atom is involved in this center.

Next we discuss the results of external field perturbation measurements, which reveal the symmetry of the center and the origin of the luminescence transitions. Both the zero-phonon lines split into 2, 3, and 4 components under uniaxial stresses along $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ directions, respectively [7]. The relative amplitudes of the peaks do not depend on temperature, which strongly sug-

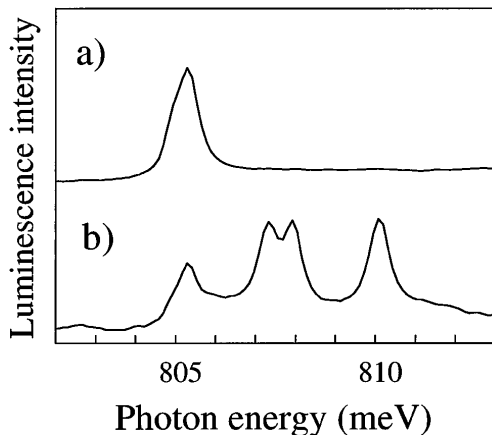


FIG. 2. PL spectra of the L_5 local vibrational mode feature from material containing (a) $^{12}\text{C} + \text{H}$ and (b) $^{12}\text{C} + ^{13}\text{C} + \text{H}$.

gests that the splitting of the line is due to the lifting of orientation degeneracy. The number of components and the absence of thermalization suggest that the symmetry of the center is monoclinic I [11]. This is not in agreement with the results of earlier study [6], where a smaller number of split components was observed, probably due to the lower spectral resolution employed. Temperature-controlled measurements have shown that with increasing temperature in the range 20–60 K, the PL intensity decays with an activation energy of 32 meV, which is much smaller than the total binding energy of the electron-hole pair, ≈ 235 meV. This is consistent with the T -line luminescence being related to the recombination of an exciton bound to a neutral center, where one particle is bound into a deep level state and the other is weakly bound in the Coulomb potential produced by the first. The thermal dissociation of the bound exciton and PL decay, in this case, is associated with an excitation of the weakly bound particle to the nearest band. A detailed analysis of the uniaxial stress and magnetic field measurements has shown that the shallow effective-mass-like particle in the bound exciton is a hole, contrary to a previous suggestion [6], and consequently the defect possesses a deep acceptor level ($-/0$) at 0.2 eV below the conduction band [7]. It has been found that the behavior of the hole under external field perturbations, as well as the strong anisotropy of the g tensor, can be successfully described by the characteristics of the valence band maxima, in agreement with the hole being bound by the Coulomb potential [7]. In addition, the analysis of the magnetic data has shown that the defect in its neutral ground state has an uncoupled electron with spin $\frac{1}{2}$ and a g factor close to 2. Upon photoexcitation, when an exciton is bound to the defect and an additional electron occupies the acceptor level, the two electrons are coupled in a singlet state with $S = 0$, so that the magnetic splitting of the excited state is determined by the weakly bound hole with spin $\frac{1}{2}$ and strong anisotropic g factors while the splitting of the final state is determined by the electron. This fully accounts for the observed structure of the Zeeman splitting, which corresponds to transitions between states with spin $\frac{1}{2}$ and explains the absence of thermalization between the two sublevels of the final ground state and the absence of exchange coupling between the bound exciton particles [6]. Note that the paramagnetic nature of the center in its neutral state is consistent with the presence of one hydrogen atom in the defect.

Having established the chemistry and symmetry of the center, we now describe the results of *ab initio* cluster calculations which lead us to a unique model of the defect. Details of the method and applications to substitutional carbon (C_s), interstitial carbon (C_i), and the dicarbon defect ($C_s - C_i$), as well as defects containing hydrogen, have been given previously [12–14] and will not be repeated here. A trigonal 88 atom cluster $C_2\text{HSi}_{43}\text{H}_{42}$ was used in all calculations presented here, all atoms were relaxed until the equilibrium structure was determined.

TABLE I. Comparison between calculated and (experimental) vibrational modes, cm^{-1} , for the $\langle 100 \rangle$ oriented C-(CH) and C-(CD) defects, along with their downward isotope shifts.

Sym	Mode	^{12}C -(^{12}C -H)	Δ ^{12}C -(^{13}C -H)	Δ ^{13}C -(^{12}C -H)	Δ ^{13}C -(^{13}C -H)
A		2913.6	8.3	0.0	8.3
A		1180.4	1.8	5.5	6.9
A	L_5	1097.8 (1056.0)	19.2 (18.0)	20.7 (27.0)	40.8 (45.0)
B		870.7	1.7	0.0	1.7
A	L_4	743.6 (796.0)	1.0	22.0 (25.0)	23.1 (25.0)
A	L_3	558.0 (567.5)	4.9 (7.5)	3.4 (3.0)	7.6 (10.0)
A	L_2	542.4 (531.5)	3.7 (4.0)	0.2 (2.0)	3.8 (5.5)
Sym	Mode	^{12}C -(^{12}C -H)	Δ ^{12}C -(^{13}C -H)	Δ ^{13}C -(^{12}C -H)	Δ ^{13}C -(^{13}C -H)
A		2138.3	12.1	0.0	12.2
A	L_5	1102.2 (1052.0)	17.1 (16.5)	24.3 (20.5)	42.3 (38.0)
A		892.6	4.5	8.1	12.5
A	L_4	713.7 (759.0)	0.9	16.6 (16.5)	17.3 (16.5)
B		643.6	4.0	0.2	4.2
A	L_3	552.7 (558.5)	4.0 (5.3)	2.7 (2.5)	6.1 (7.7)
A	L_2	539.2 (528.0)	2.5 (1.3)	0.1 (-1.8)	2.5 (2.3)

The second derivatives of the energy with respect to atomic positions were calculated for the C and H atoms, as well as their nearest Si neighbors. Energy second derivatives for the remaining atoms were taken from the Musgrave-Pople potential found by a previous *ab initio* calculation [15], and the dynamical matrix of the cluster, and hence its vibrational modes, were calculated.

We first note that the C-related L_5 mode at 1056 cm^{-1} lies within 130 cm^{-1} of modes due to C_i and more than 400 cm^{-1} above those of C_s [16]. This suggests that the T center contains C_i . We now argue that the observed C-isotope shifts of the L_5 mode suggest the presence of a C-C bond. This follows as the reduced mass of an isolated C-C unit implies that its stretch frequency would shift downwards by 20, 20, and 41 cm^{-1} for ^{13}C - ^{12}C , ^{12}C - ^{13}C , and ^{13}C - ^{13}C , respectively. These shifts roughly agree with the observed values of 18, 27, and 45 cm^{-1} for the H case, and 16.5, 20.5, and 38 cm^{-1} for D. The different shifts in the two mixed C-isotope cases imply that the C atoms are inequivalent, and the distinct shifts in the H and D cases suggest that H is bonded with one of the C atoms. Thus we look for models with C_{1h} symmetry containing C_i and C-C-H units.

Several models were examined [17], and the ground state structure was found to be the one shown in Fig. 3 where a $\langle 100 \rangle$ oriented C-C pair share a substitutional site. The H atom is attached to one of the carbon atoms, denoted C_4 , and the second undercoordinated carbon atom is labeled C_3 . The calculations show that the C_3 - C_4 , C_4 -H, C_3 -Si, and C_4 -Si bond lengths are 1.46, 1.11, 1.91 (2), and 2.05 (2) Å, respectively. The calculated vibrational modes and their isotope shifts are given in Table I. Now, PL only detects modes of A symmetry, and we concentrate on those at 2913, 1180, 1098, 744, 558, and 542 cm^{-1} . The first four modes correspond predominantly to C_4 -H stretch, C_4 -H wag, C_3 - C_4 stretch, and C_3 -Si stretch, respectively. The last two modes at

558 and 542 cm^{-1} are close to the Raman frequency, and involve predominantly the motion of C_3 and C_4 , respectively, as well as their Si neighbors. There is close agreement between the modes L_2 to L_5 observed by PL and the calculated vibrational modes which enables them to be identified (Table I). The two highest energy modes at 2913 and 1180 cm^{-1} are undetected by PL. However, the intensities of the phonon-assisted transitions are critically dependent on the exciton-phonon coupling, and not necessarily all local modes can be detected by PL. In addition, there is an experimental problem in observing the highest energy local mode since the Ge detector is insensitive in the region where the position of the corresponding luminescence line is expected. The C_3 - C_4 stretch mode lies close to L_5 and has carbon isotope

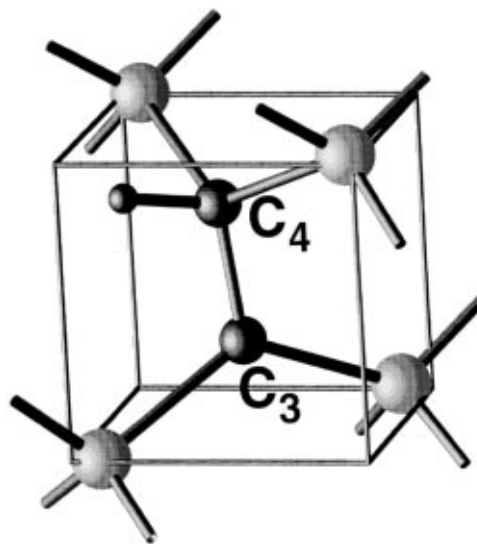


FIG. 3. The proposed structure of the defect giving rise to the T center.

shifts 19, 21, 41 cm^{-1} in the H case and 17, 24, 42 cm^{-1} in the D case. These shifts are in good agreement with the experimental values 18, 27, 45 cm^{-1} and 16.5, 20.5, 38 cm^{-1} , respectively, observed for L_5 . We therefore identify the L_5 mode with C_3 - C_4 stretch. The C_3 -Si stretch mode at 744 cm^{-1} involves the movement of H as well, but has little amplitude on C_4 . As a consequence, this mode displays large isotope shifts with both ^{13}C and D—23 cm^{-1} and 30 cm^{-1} , respectively—but essentially no additional modes appear in the mixed C-isotopic cases. These results allow us to identify the mode with L_4 at 796 cm^{-1} , which decreases by 25 and 37 cm^{-1} for ^{13}C and D, respectively, and involves the motion of only one of the C atoms. Finally, the two lower A modes at 558 and 542 cm^{-1} (H) are in good agreement with L_3 and L_2 , at 567.5 and 531.5 cm^{-1} , respectively. These modes are more delocalized and have only small shifts with D and the various combinations of the C isotopes.

The neutral defect has a deep midgap donor level occupied by one electron, although the theory is unable to locate it exactly. This donor level has not been reported so far. The acceptor level at $E_c - 0.2$ eV would then be explained by a large Hubbard- U term of at least 0.4 eV. The structure and electronic properties of the center are similar to the stable form of the P- C_i defect which possesses acceptor and donor levels at $E_c - 0.38$ eV and $E_v + 0.48$ eV, respectively [18].

The wave function for the singly occupied level is localized on a nonbonding p orbital on the C_3 atom and has spin $\frac{1}{2}$ in agreement with the Zeeman measurements described above. Only small isotropic hyperfine couplings with C_4 and H are, however, to be expected. The saturation of the dangling bond related to C_3 by a second H atom would eliminate the optical activity of the center, which might account for the observed loss of the PL intensity when the H concentration is large [3,4].

The calculations presented here favor the $\langle 100 \rangle$ oriented C_3 - C_4 -H split-interstitial as a candidate for the T center, although additional support would arise from observations of the C-H stretch and wag modes at 2914 and 1180 cm^{-1} , as well as the mode of B symmetry. The presence of a C-C bond is surprising as the C_i - C_s defect, which is stable to about 300 °C, and only contains C-Si bonds [19]. We suggest that the T center is formed when C_i traps H in the BC sited defect. This in turn diffuses to C_s where conversion to the T center takes place. A calculation shows the trapping of C_i -H by C_s leads to an energy reduction of 1.4 eV [17]. This formation mechanism is more likely than the trapping of H by the dicarbon defect as the latter is not stable at 400–600 °C.

The identification of this defect is important for several reasons. It is commonly produced in FZ and CZ silicon samples after irradiation and heat treatment, showing that H is present as an unintentional impurity in silicon [2,3]. The defect structure and the mechanisms of formation

provide further evidence that thermal treatment of CZ Si leads to a generation of Si_i , which can be subsequently trapped by C_s to produce mobile C_i . The stability of the T center over an important temperature range (400–600 °C) where thermal donors are generated may enable it to be used to monitor Si_i production. The results reported in this paper show that the presence of hydrogen can lead to the formation of unusually stable electrically and optically active defects.

In conclusion, a combination of high resolution photoluminescence experiments, Zeeman and uniaxial stress studies, and *ab initio* theory have successfully elucidated the structure and properties of an interstitial carbon-hydrogen defect in silicon.

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