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Dynamic properties of interstitial carbon and carbon-carbon pair defects in silicon

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Interstitial carbon, C_i, defects in Si exhibit a number of unexplained features. The C_i defect in the neutral charge state gives rise to two almost degenerate vibrational modes at 920 and 931 cm^{-1} whose 2:1 absorption intensity ratio naturally suggests a trigonal defect in conflict with uniaxial stress measurements. The dicarbon, C_s-C_i, defect is bistable, and the energy difference between its *A* and *B* forms is surprisingly small even though the bonding is very different. In the *B* form appropriate to the neutral charge state, a silicon interstitial is believed to be located near a bond-centered site between two C_s atoms. This must give rise to vibrational modes which involve the motion of both C atoms in apparent conflict with the results of photoluminescence experiments. We use an *ab initio* local density functional cluster method, AIMPRO, to calculate the structure and vibrational modes of these defects and find that the ratio of the absorption intensities of the local modes of C_i is in reasonable agreement with experiment even though the structure of the defect is not trigonal. We also show that modes in the vicinity of those detected by photoluminescence for the *B* form of the dicarbon center involve independent movements of the two C atoms. Finally, the trends in the relative energies of the *A* and *B* forms in three charge states are investigated. [S0163-1829(96)05848-1]

I. INTRODUCTION

Carbon is a common and important impurity in silicon, typically occurring in concentrations of around 10^{16}–10^{18} cm^{-3}, and predominantly occupying substitutional sites, C_s. Upon irradiation, mobile silicon interstitials (Si_i) can be captured by C_s, forming the interstitial carbon defect C_i.[1–11] The defect is characterized by two local vibrational bands, at 920 and 931 cm^{-1}, whose absorption intensities are in a ratio of approximately 2:1. This suggested to the earliest workers a trigonal defect.[2] However, later work with lightly irradiated *p*-type Si was able to correlate an electron paramagnetic resonance (EPR) spectrum with the infrared absorption. The EPR showed that C_i^+ possessed C_{2v} symmetry.[4] The hyperfine splitting on ^{13}C showed that the highest occupied state in C_i^+ consisted of a localized *p* orbital centered on the C atom. Deep level transient spectroscopic (DLTS) measurements gave a donor level at $E_v+0.28$ eV. These results suggested a model of the defect shown in Fig. 1.

More recent EPR and DLTS investigations on *n*-type material[5] found an acceptor level at $E_c-0.10$ eV and that C_i^- also possessed C_{2v} symmetry. The similarity between the reorientation barriers of the defects in both charge states ($\approx$0.8 eV) indicated that they possess the same structure. However, no hyperfine splitting of the EPR line due to C_i^- with ^{13}C or ^{29}Si was observed, possibly because the partially occupied acceptor state is extended over a number of Si atoms and has only a small overlap with carbon.

The defect is associated with an 856 meV photoluminescence (PL) line and uniaxial stress measurements revealed that the symmetry of the defect was also C_{2v} (monoclinic I).[6] It is just possible that the neutral defect possesses trigonal symmetry and reorients to C_{2v} in a charged state when a carrier is thermally trapped before radiative recombination occurs. However, unambiguous confirmation that the symmetry of the neutral defect is indeed C_{2v} and not trigonal came from the response of the two local vibrational modes (LVMs) of the neutral defect to uniaxial stress.[7] These experiments showed that the symmetries of the 920 and 931 cm^{-1} LVMs were A_1 and B_1, respectively. Thus it appears that

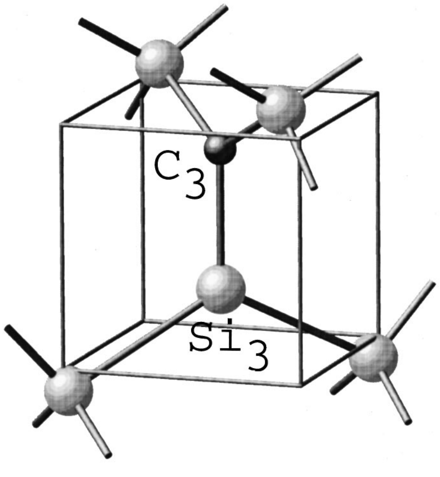

FIG. 1. The ground state configuration of the interstitial carbon defect in Si. The atoms with reduced coordination numbers are marked.

TABLE I. Structural data of the C_i and C_i-C_s defects in Å. Here, the subscripts indicate the coordination of the atoms involved, with reference to Figs. 1–3, and (2) refers to the multiplicity of the bond.

	C_3—Si_3	C_3—Si_4	Si_3—Si_4	$\theta_{Si_4—C_3—Si_4}$	$\theta_{Si_4—Si_3—Si_4}$
C_i Ref. 11	1.77	1.80 (2)	2.22 (2)	157°	122°
C_i this work	1.728	1.820 (2)	2.300 (2)	137°	125°

	C_4—Si	C_4—Si_3	C_3—Si_3	C_3—Si	Si_3—Si
C_i—C_s *A* form	2.007 (2) 2.075	1.846	1.708	1.855 (2)	2.352

	C—Si	C—Si_2	$\theta_{C—Si_2—C}$
Ci—*C*s B form	1.960 (2) 2.330 2.043 (2) 1.970	1.831 1.819	126°

the defect adopts the structure shown in Fig. 1 in all three charge states and consists of a C and Si atom sharing a single lattice site with a ⟨100⟩ orientation.[4,5,7] However, this model gives no natural explanation of the near degeneracy of the local vibrational modes of the defect, or their 2:1 ratio in absorption intensities.

Several theoretical calculations have been performed on the C_i defect, all finding the ⟨100⟩ structure to be the ground state configuration.[8–12] Reference 9 uses several semiempirical techniques to calculate the properties of carbon defects. The calculated vibrational modes of the various defect configurations[9] provide further evidence for the C_{2v} configuration in Fig. 1. For this model they were 1005 cm^{-1} and 853 cm^{-1} for the A_1 and the B_1 modes, respectively, in fair agreement with experiment. None of the three possible C_{3v} symmetry configurations possessed two high frequency modes.

The energy barrier to reorientation of the defect among the equivalent ⟨100⟩ orientations has been calculated by Tersoff.[10] He found this to be 0.7 eV for a saddle point where the C atom lies at a bond-centered (BC) site along ⟨111⟩. This is in good agreement with experimental reorientation and migration barriers around 0.8 eV.[4,5,13] More recent calculations on the migration/reorientation barriers of the defect have calculated these to be 0.51 eV via a saddle point with C_2 symmetry[11] and 0.77 eV via a *H* site.[12] The migration/reorientation pathway considered by Capaz, Dal Pino, and Joannopoulos[11] involved a low energy, 0.51 eV, fourfold-coordinated carbon atom at the saddle point. This path involves C moving through the lattice and at the same time reorienting and hence explains why the barriers to migration and reorientation are the same. The path via a BC defect was also considered but they found it involved a 2.5 eV barrier which is considerably greater than that found by Tersoff. The structural data from this recent *ab initio* supercell calculation[11] for the neutral defect are given in Table I.

The dicarbon defect C_i-C_s is formed when Si:C, containing a low oxygen content, is *e* irradiated at room temperature, creating mobile C_i defects which are subsequently trapped by C_s.[1] The defect is bistable, taking the *A* form in the charged states and the *B* form in the neutral one. EPR and DLTS studies[14] showed that $(C_i$-$C_s)^{\pm}$ defects possessed C_{1h} symmetry, and they gave rise to acceptor and donor levels at $E_c-0.17$ and $E_v+0.09$ eV. The EPR data also found that the carbon atoms were inequivalent, and the *g* tensors were perturbed by stress in a very similar way to those of the charged C_i defect. The model proposed from the experimental data is very similar to that of C_i, the symmetry being lowered by the presence of a second carbon atom at a substitutional site shown in Fig. 2. This configuration of the C_i-C_s defect is known as the *A* form, and is the stable configuration for both singly ionized states.

For high *e*-irradiation fluences, the Fermi level is around midgap and the neutral *B* form of the defect is formed.[14,15] This state is diamagnetic, but an excited triplet state B^* has been observed by optically detected magnetic resonance (ODMR).[16] This revealed that the symmetry of the *B* form is C_{3v} for $T>$ 30 K, and C_{1h} otherwise. Hyperfine interactions on ^{13}C detected by ODMR indicated that the carbon atoms are nearly equivalent. DLTS studies on the metastable $B^{\pm}$ form, which has trapped a carrier, show that it has shallow donor and acceptor levels at $E_v+0.07$ and $E_c-0.11$ eV, respectively. It has also been possible to observe EPR from the metastable B^- form, but not from B^+. B^- is also found to have C_{3v} symmetry for $T>$ 15 K and again C_{1h} below this temperature. The ODMR results suggest that the two C atoms lie close to neighboring substitutional sites, with a sili-

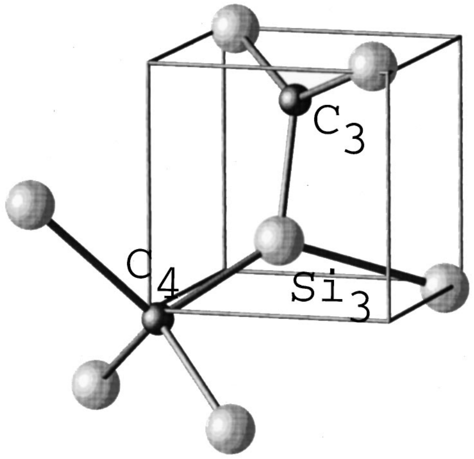

FIG. 2. The *A* form of the dicarbon defect. The defect can be thought of as a C_i defect bound to a substitutional carbon atom.

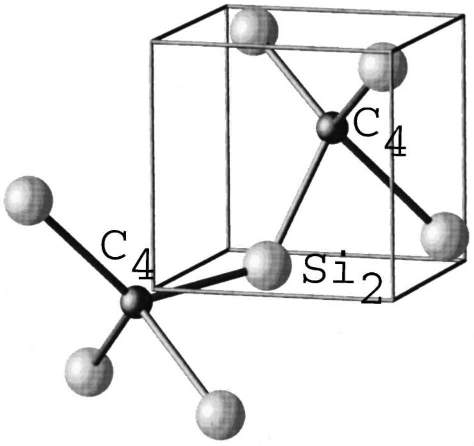

FIG. 3. The *B* form of the dicarbon defect. This defect is a bond-centered silicon atom lying between two substitutional carbon atoms.

con interstitial, Si_i, close to a BC site lying between them. This configuration is illustrated in Fig. 3.

There are three peculiar features with this model. First, if Si_i lay at the BC site, then the resulting D_{3d} symmetry would give a partially occupied *e* level. This would probably be split through a Jahn-Teller distortion, resulting in Si_i moving away from the BC site. However, the distortion cannot be too great if the reorientation energy around the C-C axis is to remain small. Nevertheless, the observed donor and acceptor levels are split by 0.97 eV, whereas a small distortion would lead to a difference in donor and acceptor levels of at most 0.5 eV, which is an estimate for the Hubbard *U*-correlation energy. On the other hand, if the distortion is not small, then the reorientation energy might be substantial and the symmetry of the defect would not be C_{3v}.

A second difficulty comes from the vibrational modes of the defect. The *B* form gives rise to a zero phonon luminescence line at 969 meV. The fine structure associated with this line reveals two local vibrational modes, at 543.0 and 579.5 cm^{-1} (^{12}C), which shift by 10.1 and 14.9 cm^{-1}, respectively, for ^{13}C samples. However, in a sample containing a mixture of ^{12}C and ^{13}C, additional lines are observed which are shifted only by 0.1 and 0.6 cm^{-1}. Indeed, the original PL investigations failed to find distinct modes in the mixed case, and incorrectly suggested that the defect only contained one C atom. These tiny shifts confirmed that two carbon atoms were present in the defect, but implied that they are almost dynamically decoupled.[17,18] It has been suggested that this decoupling arises because the two C—Si_i bonds are almost orthogonal to each other.[14] Even if this were the case, it would require that the C—Si_i stretch modes lie around 550 cm^{-1}. This is unlikely since the reduced coordination of Si_i will result in a shorter C—Si_i bond, and hence the C—Si_i stretch should be larger than the highest mode of C_s, which occurs at 607 cm^{-1}.[19]

A third peculiarity is that the positive and negative charge states of the *B* form are metastable, with energy differences with the *A* form of only a few hundredths of an eV in all three charge states. Similarly, the barriers between the forms are only 0.1–0.2 eV. As the bonding in the two forms is quite different and bond energies are of the order of 1 eV, it is surprising that these energy differences are so small.

Theoretical modeling of the dicarbon defect is still in its early stages, and to date three groups have examined the center.[9,12,24] The first two focused on the relative energies of the *A* and *B* forms, and in our previous work, we analyzed local modes of the *B* form only. The findings of the previous calculations relating to the defect energies are summarized in Table IV.

We discuss the standard models, and analyze their structure and vibrational modes in this paper. The method is discussed in Sec. II, and applied to the C_i defect in Sec. III and the dicarbon center in Sec. IV. We give our conclusions in Sec. V.

II. METHOD

The calculations presented here were performed using an *ab initio* local density functional cluster method on large H-terminated clusters (AIMPRO). A C atom was inserted into the central region of a 71 atom tetrahedral cluster $Si_{35}H_{36}$ to investigate the structure of C_i. The migration energy of C_i was found by inserting a C atom into a trigonal 86 atom cluster $Si_{44}H_{42}$, oriented along $\langle 111\rangle$. A central Si atom was then replaced by C to investigate the dicarbon defect. Norm-conserving pseudopotentials for C and Si were taken from Ref. 20.

The electronic wave functions were expanded in *s* and *p* Gaussian orbitals, centered on nuclei and the center of all bonds. The basis used here for the structural and local mode calculations was as follows: eight Gaussian fitting functions of different exponents were used on the carbon atom(s) and inner silicon atoms, and a fixed linear combination of eight Gaussians were placed on the remaining Si atoms. A linear combination of three Gaussians were used for the terminating hydrogens. Additionally, three *s* and *p* Gaussian orbitals were placed at the center of every C—Si and Si—Si bond.

The electron charge density was fitted in exactly the same way as the wave functions. The self-consistent energy was then found, and the forces on each atom calculated. The whole structure is then relaxed using a conjugate gradient algorithm, until the equilibrium structure is determined. To explore the saddle points needed for migration energies, the relative bond lengths of the carbon atom were constrained during the relaxation as discussed previously.[21] The second derivatives of the energy with respect to atomic positions were calculated for the carbon atom(s) and their neighboring Si atoms. Energy second derivatives for the remaining atoms were taken from the Musgrave-Pople potential found previously,[22] and the dynamical matrix of the cluster then constructed. From the dynamical matrix, the vibrational modes and their normal coordinates $u_{l,i}$ can be calculated.

We have previously shown that the dipole moments for small molecules can be found accurately using this method,[23] and this can be used to evaluate the effective charge η associated with the vibrational modes of the defect. However, a larger basis is required for the accurate determination of η so in this calculation the number of Gaussians used to fit the wave function and charge density of C and Si was increased to 10. It is the effective charge which controls the intensity ratio of the two infrared (IR) absorption lines. In this work, η is calculated for the two highest local vibrational modes of

TABLE II. Experimental and calculated LVMs, cm^{-1}, of the Cidefect, and their downwards isotope shifts.

	A			B		
	^{12}C	^{13}C	^{14}C	^{12}C	^{13}C	^{14}C
Experiment	921.0	29	54	930.3	26	49
Theory	922.2	28	52	866.9	28	52

C_i, having A_1 and B_1 symmetries. These modes largely involve motion of the carbon atom along [001] and [110], respectively, together with movements of the Si neighbors. η is found by calculating the change in the adiabatic dipole moment of the cluster, when the atoms of the cluster are displaced by $\pm u_{l,i}/\sqrt{M_i}$. Here M_i is the mass of the displaced atom.

III. THE C_i DEFECT

Previous theoretical modeling studies[8–11] have found that the ground state configuration is the [100] C—Si split interstitial, with C_{2v} symmetry, as illustrated in Fig. 1. We therefore take this structure as the starting point, and relaxed all atoms of the 72 atom cluster containing the defect shown in Fig. 1 in various charge states.

Details of the structure found for C_i are given in Table I and compare favorably with a previous *ab initio* calculation.[11] For the neutral defect, the C atom made strong bonds with the Si atom, labeled Si_3, along the [100] axis and slightly weaker bonds with its neighboring Si atoms, labeled Si_4, along [011]. Nevertheless, the C atom pulls in the Si_4 neighbors along this direction leaving the Si_4—Si bonds along [011] slightly stretched at 2.352 Å. The Si_4—C—Si_4 and Si_4—C—Si_3 bond angles are 137° and 125°.

There are two high frequency modes, at 922.2 (A_1) and 866.9 (B_1) cm^{-1}, which decrease by 27.6 and 27.8 cm^{-1}, respectively, with ^{13}C. These frequencies are in fair agreement with the experimental results (Table II) of 921 and 930 cm^{-1}—although the ordering of the modes is given incorrectly. The calculated isotope shifts are in very good agreement with the experimental results, with a decrease of 28.8 and 25.8 cm^{-1} for the A_1 and the B_1 modes, respectively. These results are similar to those of Ref. 9, where again, the ordering of the LVMs was given incorrectly.

The separation of the two vibrational modes is much greater than experiment and is very sensitive to the C—Si bond lengths.[24] If the length of the C—Si_4 bond is reduced by 2% then the modes become 926 cm^{-1} (A_1) and 950 cm^{-1} (B_1) and the ordering is now in agreement with experiment. In fact, the 1% difference in the experimental frequencies suggests that the C—Si bond lengths can differ by no more than 0.03%.[25]

We then investigated the structure of the negatively charged defect. Adding an electron and relaxing all the atoms of the cluster, without any restriction, causes the three C—Si bond lengths to become almost equal: the C—Si_3 and C—Si_4 bonds becoming 1.788 and 1.805 (2) Å, respectively, where (2) refers to the multiplicity of the bond. The Si_4—C—Si_4 bond angle decreased slightly to 136.0°, and the Si_4—Si bond length decreased slightly to 2.238 Å. The resulting vibrational modes have now crossed over with an ordering in agreement with experiment. The A_1 mode has decreased to 840.98 cm^{-1} with a corresponding increase of the B_1 mode to 901.78 cm^{-1}. So, once again the near degeneracy of these modes seems to arise from an equality in the three Si—C bonds. In this case, if the C bond angles were 120°, the C atom and its three Si neighbors would then make a molecule with a C_3 axis along [011]. This would then automatically give a twofold degenerate E vibrational mode.[24] This symmetry would, however, also imply that the infrared intensities of the two modes are equal, which is contrary to experiment. The effective charges for the highest two local modes of the fully relaxed neutral defect were then calculated from the change in the cluster dipole moment with the atoms displaced according to the normal coordinates. The effective charges were found to be $\eta_{A_1}=0.88|e|$ and $\eta_{B_1}=0.68|e|$. The IR intensity ratio of the local modes is given by $(\eta_{A_1}/\eta_{B_1})^2$, and results in a ratio in the range (1.5–1.7):1, in reasonable agreement with the experimental ratio of 2:1 with the A_1 mode being the more intense in agreement with observation. For the negatively charged defect, we find the intensity ratio to be in the range (1.4–1.5):1. Thus although the symmetry of the core of the defect is almost trigonal and the two LVMs transform as E, the departure from symmetry is sufficient to lead to quite distinct induced dipole moments.

We now discuss the electronic structure of the defect. Although the energy levels are only given approximately by the theory, we use them along with the pseudo-wave-functions for a qualitative analysis of the zero phonon transition. The Kohn-Sham eigenvalues indicated that there are at least two, possibly three, defect-related levels in the band gap. The highest occupied state has b_1 symmetry, and in agreement with EPR (Ref. 4) it corresponds to a non-bonding p orbital on carbon [Fig. 4(b)]. This lies above an a_1 level whose wave function, Fig. 4(a), has little amplitude on C, and is mainly localized over the Si atoms neighboring C atoms. The first unoccupied state shown in Fig. 4(c) has b_2 symmetry, and is diffusely localized over the three Si neighbors of C, predominantly on Si_3 but with little amplitude on carbon. Again, this is in agreement with the EPR data on the ionized donor and acceptor states.[5] The level above the b_2 level has a_1 symmetry, and is delocalized and probably part of the conduction band. The 856 meV zero phonon line transition might be either due to an electron in the upper a_1 state recombining with a hole trapped in the b_1 state associated with the nonbonding p orbital on C, or, alternatively an electron in the upper b_2 state recombining with a hole in the lower a_1 state. Most workers have considered it to be the former process, involving the b_1 state localized on carbon.[26] This seems to us unlikely because the PL has no fine structure, and the zero phonon line is unaffected by substitution of ^{13}C.[27] This implies that the bonding of carbon is unchanged as a result of the transition. If the C atom relaxed as a consequence of a hole occupying the C-related b_1 state—as indicated by the calculations—then an isotope shift would be expected. We therefore suggest that the observed PL involves the latter transition, which involves the diffusely localized states. This would imply that the dipole for the PL transition is at right angles to the p orbital on the carbon atom.

The energies for migration/reorientation of the defect

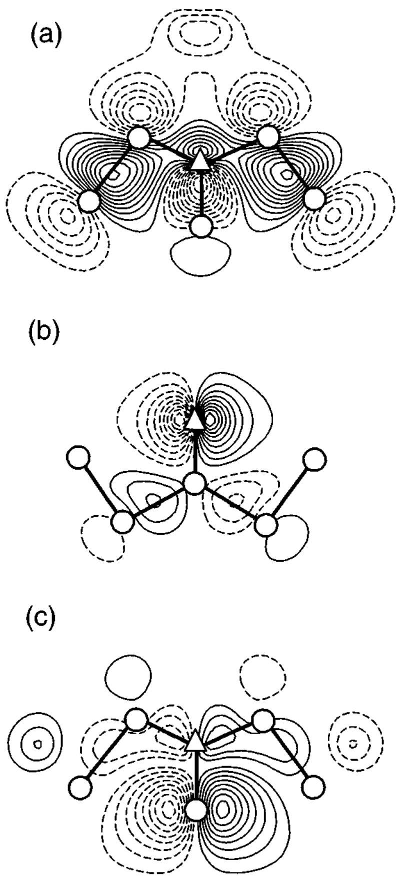

FIG. 4. The pseudo-wave-functions of the carbon interstitial defect in Si. The white triangle represents the carbon atom, and its nearest Si neighbors are represented by white circles. (a) Wave function of second highest occupied state, (110) plane, (b) wave function of highest occupied state (110) plane, (c) wave function of lowest unoccupied state (110) plane.

were also calculated for the trajectories considered by Capaz *et al.* using a relaxation procedure with constraints. In contradiction to this work, we find that both the C_2 and bond-centered saddle points have almost equivalent barrier heights, with an energy of 1.10 eV. We therefore conclude that both are viable paths for the migration/rotation of C_i. The 1.10 eV barrier is in fair agreement with the experimental results of between 0.73 and 0.87 eV for both migration and reorientation.

In summary, the calculations yield a structure which has approximately equal C—Si bonds and gives two almost degenerate modes around 920 cm^{-1}, the near degeneracy in modes being attributed to an approximate trigonal symmetry. However, the deviation from this symmetry cause the two modes to have different absorption strengths. The migration energy of the defect is low with the C atom being either twofold or fourfold coordinated at the saddle point.

IV. THE DICARBON DEFECT

All atoms of an 87 atom cluster $C_2Si_{43}H_{42}$ containing two substitutional C atoms between which a Si_i is sited were allowed to relax. This corresponds to the *B* form of the dicarbon defect shown in Fig. 3. The Si_i moved away from the bond-centered site, with the carbon atoms moving slightly from their substitutional sites until the equilibrium structure was obtained. The bonding in the equilibrium structure is given in Table I. The C—Si_i—C angle is 126° showing that the Si_i has moved well away from a bond-centered site. This leads to a great splitting in the two gap Kohn-Sham levels and is consistent with the large donor-acceptor level difference.

TABLE III. Experimental and calculated LVMs, cm^{-1}, and their downwards isotope shifts of the *B* form of C_i-C_s.

Symmetry	^{12}C-^{12}C	^{12}C-^{13}C	^{13}C-^{12}C	^{13}C-^{13}C
A	837.9	14.1	6.3	22.1
A	714.8	10.7	13.8	23.1
B	648.7	0.0	18.4	18.4
A	582.3	12.2	2.3	14.1
B	551.8	8.6	0.1	8.8
A	543.2	0.2	4.7	4.7
A	532.2	0.3	0.4	0.5
Observed (Ref. 26)				
A	579.5	0.6		14.9
A	543.0	0.1		10.1

The local vibrational modes of this defect are given in Table III. It is clear that the *B* form must give rise to six local modes—two of which are *A* modes due to asymmetric and symmetric stretch of the C—Si_i. These modes must be of high frequency, simply because the reduced coordination of Si_i must result in stronger C—Si_i bonds. The remaining four modes involve predominantly the motion of the C atoms together with their Si neighbors. If the Si_i was at the bond-centered site, these would correspond to two degenerate *E* modes in a D_{3d} defect, but are split into four with the lower C_{1h} symmetry resulting from the displacement of Si_i.

We find six modes above the Raman peak, ranging from 543 to 838 cm^{-1}. The C—Si_i stretch modes occur at 838 and 715 cm^{-1} and these shift by 22 and 23 cm^{-1} with pure ^{13}C, but pronounced shifts occur in the mixed isotope case. The shifts of these modes in the mixed case reflect the fact that the two carbon atoms are almost equivalent in this configuration. The magnitude of these modes, and the fact that they exhibit mixed splitting, clearly rules them out as being responsible for the modes observed by PL.

The next four modes involve mainly the C atoms and their backbonded neighbors, with little motion of Si_i. The 649 and 552 cm^{-1} modes are decoupled with one carbon moving along [011] in each mode. However, these modes are of *B* symmetry, and therefore would not be detected by PL. The final two local modes are of *A* symmetry, occurring at 582 and 543 cm^{-1}, and represent vibrations in which each C atom moves independently against its Si neighbors, but not including Si_i. These modes shift by 14 and 5 cm^{-1} with pure ^{13}C, but the additional modes in the mixed isotopic case are all within 2 cm^{-1} of the pure modes. Therefore these modes are essentially decoupled, and are in excellent agreement with those found by PL. This gives two *A* modes at 579 and 543 cm^{-1} with shifts 15 and 10 cm^{-1} for pure ^{13}C. No further vibrational modes are observed experimentally, which raises the question as to why the highest two calculated *A* modes are not detected. Now, PL does not necessar-

TABLE IV. Relative total energies (eV) for the *A* and *B* forms of the dicarbon defect with varying charge state, NF indicates a structure was not found.

	A^+	B^+	A^0	B^0	A^-	B^-
Experiment[a]	0.000	0.020	0.020	0.000	0.000	0.040
Previous calculation[b]						
MINDO/3-Si_{38}	0.000	0.621	0.337	0.000		
MINDO/3-Si_{41}	0.000	0.383	0.508	0.000		
MNDO-Si_{38}	NF	0.000	0.000	1.151		
MNDO-Si_{41}	0.000	1.086	3.501	5.127		
PM3-Si_{38}	0.596	0.000	1.903	0.000		
PM3-Si_{41}	0.737	0.000	1.816	0.000		
Previous calculation[c]						
			0.800	0.000		
Present results						
	0.000	0.428	0.000	0.346	0.000	0.500

[a] Reference 14.
[b] Reference 9.
[c] Reference 12.

ily detect all *A* modes of a defect, for example, in the C_i defect, discussed above, the *A* mode at 921 cm^{-1} is not detected as a replica of the 856 meV zero phonon line. However, IR studies on the dicarbon defect have also failed to find any local modes. A possible explanation as to why these higher modes are not detected is that they have very short lifetimes. The energy of these modes, $\approx$ 0.1 eV, is comparable to the activation barrier for the conversion from the *B* form to the *A* form (0.16 eV). Since the configuration energy curves must have zero gradient at the barrier height, it suggests that the curves cannot be described by a harmonic potential much beyond 0.1 eV. We therefore suggest that anharmonic effects are considerable, leading to particularly large three phonon scattering processes which have very short lifetimes.

Investigations were also made into the *A* form of the defect, shown in Fig. 2, the equilibrium bond lengths are given in Table I. The energy difference between the two forms in the neutral charge state was found to be 0.35 eV, the *A* form being lower—a figure very much greater than the experimental difference of about 0.04 eV. It seems that accurate energy differences require a very much larger cluster as the strain fields of the two defects are very different. Although there is an offset of around 0.3 eV between our results and experiment, it is interesting to investigate the trends in energy difference between the two configurations with charge state. The *A* form was found to be lower in energy by 0.43 and 0.50 eV for both positive and negative charge states, respectively. These results are in good qualitative agreement with experiment, showing that when charged, the relative stability of the *A* form over the *B* form increases by 0.08 and 0.15 eV, compared to the experimental values of 0.04 and 0.06 eV for the positive and negative charge states, respectively. These results are given in Table IV, along with the experimental values[14] and the previous theoretical calculations.[9,12]

V. CONCLUSIONS

The calculations presented here have successfully explained some of the remaining difficulties with the structural models of the carbon and dicarbon defects. Our calculated LVMs for the C_i defect are in reasonable agreement with experiment, and the near equality of the three C—Si lengths results in the two almost degenerate local vibrational modes. The calculated infrared intensity ratio of the two LVMs gave a ratio of (1.5–1.7):1, in fair agreement with the experimental result of 2:1. The calculated energies for the migration/reorientation barriers lead to an upper bound of 1.10 eV, in good agreement with experiment.

The *B* form of the neutral C_i-C_s defect gave rise to six local modes, only two of which have been detected experimentally by PL. Two of these have very high frequency, and probably could not be detected because of large anharmonicities which would lead to a very broadened absorption. Two of these modes having A_1 symmetries lay around 560 cm^{-1}. These involved almost independent movements of the C atoms with the neighboring Si atoms, excluding the interstitial. The isotope shifts of the vibrational modes are in excellent agreement with experiment. Investigations into the relative energies of the configurations of the dicarbon defect with charge state confirms that the stability of the *A* form over the *B* form increases with charging.

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