PHYSICAL REVIEW B **77**, 205205 (2008)

C4 defect and its precursors in Si: First-principles theory

D. J. Backlund and S. K. Estreicher*
Physics Department, Texas Tech University, Lubbock, Texas 79409-1051, USA

(Received 20 February 2008; published 19 May 2008)

The irradiation of *c*-Si produces self-interstitials (Si_i), which interact with substitutional carbon to produce interstitial carbon (C_i). The latter is mobile at room temperature and interacts with interstitial oxygen (O_i) to form the C3 center (C_iO_i). If enough Si_i's are provided, C3 traps one more Si_i and forms the C4 center ($Si_iC_iO_i$). The first two defects, i.e., C_i and C_iO_i, have been abundantly studied by experimentalists and theorists alike. Their electrical, optical, and magnetic properties are very well understood. On the other hand, the C4 defect is incompletely characterized experimentally and lacks precise theoretical description. We present here the results of first-principles calculations of the configurations, binding energies, vibrational spectra, and estimated gap levels of these defects, with emphasis on the C4 center. There are three configurations of C4, labeled (a), (b), and (c). All of them exhibit vibrational modes consistent with the existing data. However, the origin of the new IR line (~ 760 cm^{-1}) associated with C4 differs: it is O related in C4(a) and C4(c) but C related in C4(b). Further, the three configurations have distinct gap levels.

DOI: 10.1103/PhysRevB.77.205205 PACS number(s): 71.55.−i

I. INTRODUCTION

Substitutional carbon[1] (C_s) and interstitial oxygen[2] (O_i) are the two most abundant impurities in as-grown float-zone (FZ) and Czochralski (CZ) Si, respectively. C_s and O_i are electrically inactive and have high activation energies for diffusion: 2.9 eV for C_s (Ref. 3) and 2.6 eV for O_i.[2] However, their interactions with radiation damage results in the formation of a range of optically and electrically active complexes.[4–6] In CZ Si, the most immediate reaction is the capture of a vacancy (V) by O_i, leading to the formation of the OV pair, better known as the *A* center.[2] In a C-rich material, the self-interstitial (Si_i) expels C_s, resulting[7,8] in the formation of interstitial carbon (C_i), which is mobile at room temperature.[7,9]

The formation of C_i triggers a series of reactions. One of them is the formation of the C_iC_s pair.[10,11] Another is the formation of the C_iO_i pair.[12,13] With increasing irradiation dose, more Si_i's are available and C_i, C_iC_s, and C_iO_i become themselves traps for self-interstitials,[14–18] leading to the formation of Si_iC_i, $Si_iC_iC_s$, $Si_iC_iO_i$ and then larger complexes.

This work focuses on the sequence $C_i \rightarrow C_iO_i \rightarrow Si_iC_iO_i$. The first two defects have been extensively studied experimentally and theoretically. Much less is understood about the third. Preliminary results of our calculations on its stable configuration are in Ref. 19.

$^{12}C_s$ is characterized[1,20,21] by a local vibrational mode (LVM) at 607.5 cm^{-1} (604 in ^{29}Si), which shifts to 589.1 and 572.8 cm^{-1} for ^{13}C and ^{14}C, respectively. This defect has no level in the gap and remains in the 0 charge state for any position of the Fermi level. Therefore, there is no magnetic or electrical signature associated with it.

C_i, known as the C1 optical[9] center, is characterized by a zero-phonon line at 856 meV with no phonon sidebands. C_i^+ and C_i^- are the G12 (Ref. 3) and Si-L6 (Ref. 22) electron paramagnetic resonance (EPR) centers, respectively. The Fourier-transform infrared (FTIR) absorption lines[9] for $^{12}C_i$ are at 922.3 and 932.3 cm^{-1}. In ^{30}Si, the LVMs associated with $^{12}C_i$ and $^{13}C_i$ are at 916.8, 924.4 cm^{-1} and 892, 904 cm^{-1}, respectively.[21,23] Deep-level transient spectroscopy (DLTS) studies[22,24,25] showed that C_i has donor and acceptor levels at $E_v+0.28$ eV and $E_c-0.10$ eV, respectively. First-principles theory predicts[26,27] that it is a split $\langle 100\rangle$ interstitialcy in all three charge states. The calculated LVMs for $^{12}C_i$ in H-saturated clusters[26] and in periodic supercells[26,27] are 922, 867 cm^{-1} and 960, 936 cm^{-1}, respectively, in relatively good agreement with the experimental values. The calculated shifts of these frequencies associated with the ^{13}C and ^{14}C isotopes are very close to the measured ones.

The C_iO_i pair, known as the C3 center,[28–30] is characterized by a zero-phonon line at 790 meV with several phonon sidebands.[31,32] $C_iO_i^+$ is the G15 EPR center.[13] It has spin 1/2 and C_{1h} symmetry. The similarities between the *g* tensors and the ^{13}C hyperfine tensors of the G15 and G12 centers imply that C is not directly bound to O.

At low temperatures, the LVMs[12,21,33] are at 1116.3, 865.9, 742.8, 588, 549.8, and 529.6 cm^{-1}. In addition, Londos *et al.*[17] reported that the IR line at 544 cm^{-1} actually consists of two lines at 543.5 cm^{-1} (associated with the C_iC_s pair) and 545.5 cm^{-1} (associated with C_iO_i). Thus, a total of seven IR lines characterize the C3 defect. The various lines shift with the C, O, and Si isotopes. These shifts have been measured and calculated.[21,34] The two high-frequency LVMs are not O but C related. This is surprising since the asymmetric stretch of isolated $^{16}O_i$ is at 1136 cm^{-1}, close to the highest-frequency LVM of C_iO_i. Since the highest O-related mode in this defect is at 743 cm^{-1}, the O atom in C_iO_i cannot be twofold coordinated as it is in isolated O_i. Finally, a donor level[35] at $E_v+0.38$ eV has also been reported, but no acceptor level has been associated with this center. Shinoda and Otha[36] proposed the existence of a precursor "$C_iO_i^*$" to the C3 defect, characterized by an electron trap at $E_c-0.06$ eV.

The C_iO_i pair has been studied theoretically using first-principles methods, first in H-saturated clusters,[37] and then in periodic supercells.[34,38,39] There is agreement that the structure of the defect has both C and O threefold coordinated, each bonded to three Si atoms. The overcoordination of O is responsible for the absence of high-frequency LVMs associated with it. The LVMs for this defect have been calculated, including the various isotope substitutions (see below). The only level in the gap[34] is a donor level, predicted to be at $E_v+0.36$ eV, i.e., a value obtained using the marker method with C_i as a marker. Finally, the calculated[34] binding energy of the pair relative to isolated O_i and C_i is 1.7 eV, a value consistent with the high annealing temperature [above 350 °C (Ref. 12)] reported experimentally.

Two IR lines at about 940 and 1024 cm^{-1} associated with the C4 center, $Si_iC_iO_i$, have first been reported over 20 years ago.[15,40,41] The isotope shifts[21,42] show that the former is C related and the latter O related. The isotope shifts are at 939.8 and 1024.2 in $^{28}Si_i{}^{13}C_i{}^{16}O_i$, 911.2 and 1012.5 in $^{28}Si_i{}^{13}C_i{}^{16}O_i$, 939.2 and 982.3 in $^{28}Si_i{}^{12}C_i{}^{18}O_i$, and 933.2 and 1017.5 in $^{30}Si_i{}^{12}C_i{}^{16}O_i$.

DLTS experiments have not associated any gap level with the C4 defect.[1] However, its creation requires rather high irradiation doses, making DLTS measurements difficult to perform.[43] Since no EPR or PL signal has been associated with C4, there is no experimental evidence of electrical activity.

Coutinho [21] finds that this center has a structure similar to that of the HC_iO_i complex (Fig. 4 of Ref. 34). The calculated LVMs for the $^{28}Si_i{}^{12}C_i{}^{16}O_i$ isotopic combination are 683, 744, 908, and 998 cm^{-1} and the calculated isotopic shifts for the two highest-frequency LVMs are in fair agreement with the observed ones.

The annealing behavior of the 940 and 1024 cm^{-1} lines was studied by two groups with conflicting results. Murin *et al.*[42] irradiated *n*-type Si samples to generate the defect, then performed isochronal annealings in 25 °C steps for 30 min from 75 to 325 °C. The LVMs were measured at 20 and 300 K. Londos *et al.*[44] also performed isochronal anneals of 20 min in 10 °C steps from room temperature to 450 °C.

Murin *et al.*[42] found that in the range of 150–200 °C, the 940 and 1024 cm^{-1} lines are transformed into three new LVMs at 724 (O related) and at 952 and 973 cm^{-1} (both C related); then, in the range of 250–275 °C, these lines disappear as new LVMs at 969 (O related) and at 951 and 977 cm^{-1} (C related) emerge. New lines at 955 and 963 cm^{-1} following 300 °C anneals were also reported by Inoue *et al.*[33] but were not assigned to a specific defect. These lines disappear at about 325 °C.

Note that during these anneals, the highest O-related LVM shifts from 1024 down to 724 and back up to 969 cm^{-1}, suggesting that the O atom is first twofold, then threefold, then again twofold coordinated. The authors proposed that three different configurations of C4 are responsible for this annealing behavior and labeled these C4, C4*, and C4**. However, this interpretation is not unique because C4 is a trap for self-interstitials.[15] Londos[45] pointed out that the di-interstitial anneals out[46] around 170 °C, thus providing a source of self-interstitials at about the right temperature. Thus, the formation of $Si_{i2}C_iO_i$ instead of a C4* defect cannot be ruled out. Further, around 300 °C, larger self-interstitial clusters become a source of self-interstitials and $Si_{i3}C_iO_i$ or even larger complexes could form instead of C4**.

Londos *et al.*[44] reported that the IR lines associated with C4 begin to disappear around 150 °C, but that no new IR lines emerge. Thus, the thermal evolution of C4 may depend on the history of the sample. Londos[45] also reported a third IR line at 760 cm^{-1}, which anneals out together with the two lines associated with C4 (which he reported to be at 924 and 1018 cm^{-1}). This new line is weak but appears in n^0 as well as e^- irradiated samples. It is not known if this line is O or C related. A rather broad IR line around 750 cm^{-1} is visible (but not discussed) in Ref. 33.

Thus, the experimental information about the C4 defect is at best incomplete. It is quite surprising that the C4 center gives rise to at most three IR lines, while the simpler C3 center produces seven lines. Two of the three lines now associated with C4 were reported over 20 years ago, while the third, weaker line was only very recently detected. C4 has been reported to anneal out into a series of other defects with specific IR signatures, as well as without the appearance of any new lines at all. Finally, it is surprising that a complicated and low-symmetry defect, which includes C_i, O_i, and Si_i, exhibits no electrical activity.

The main goal of the present study is to investigate the stable and metastable configurations of the C4 center and predict its properties: binding energy, vibrational spectrum, and gap levels. However, we also summarize the results of our calculations for the simpler C_s, C_i, and C_iO_i defects in order to establish the validity of our approach and estimate our error bars.

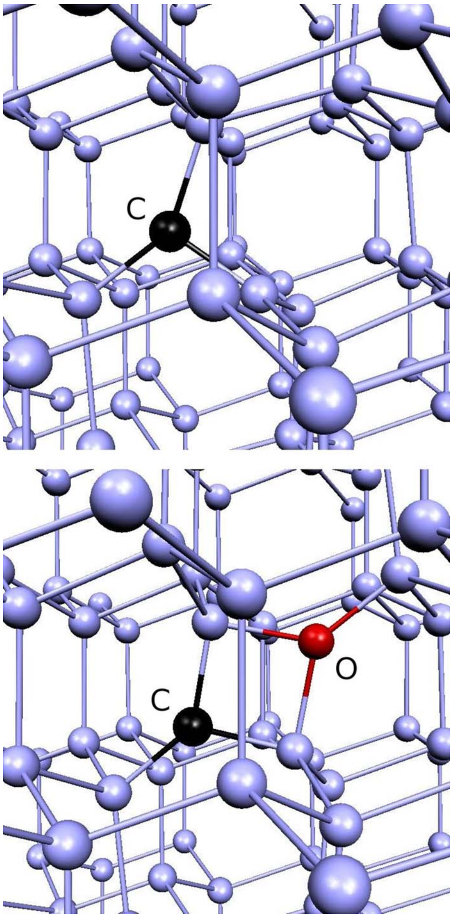

FIG. 1. (Color online) Structures of C_i and C_iO_i.

The level of theory is discussed in Sec. II. Our results for the C_s, C_i, and C_iO_i defects are compared to other predictions and to the experimental data in Sec. III. Section IV discusses the stable and metastable configurations of C4. The key results are discussed in Sec. V.

II. METHODOLOGY

Our first-principles density-functional calculations are carried out using the SIESTA package[47,48] within the local density approximation to the exchange-correlation potential.[49] The host crystal is represented by a 128 host atoms periodic supercell. A $3\times3\times3$ Monkhorst–Pack[50] mesh is used to sample the Brillouin zone except for dynamical matrices, which are calculated at the Γ point. Norm-conserving pseudopotentials in the Kleinman–Bylander form[51] are used to remove the core regions from the calculations. The valence regions are treated with the exchange-correlation potential of Ceperley–Alder[52] as parameterized by Perdew–Zunger.[53] The basis sets for the valence states (double zeta for C and O and double zeta with polarization functions for the Si atoms) are linear combinations of numerical atomic orbitals of the Sankey type.[54] The charge density is projected on a real-space grid with equivalent cutoffs of 150 Ry to calculate the exchange-correlation and Hartree potentials.

The geometries are optimized using a conjugate gradient algorithm. The dynamical matrices are calculated at the Γ point within linear-response theory.[55–57] The eigenvalues are the normal-mode frequencies ω_s. The orthonormal eigenvectors $e^s_{\alpha i}$ $(i=x,y,z)$ give the relative displacements of the nuclei α for each mode s. A quantitative measure of how localized a specific mode is on one atom or a group of atoms is provided by a plot of $L^2_{\{\alpha\}}=(e^s_{\alpha x})^2+(e^s_{\alpha y})^2+(e^s_{\alpha z})^2$ vs s or ω_s. Here, $\{\alpha\}$ may be a single atom or a sum over a group of atoms. Such a *localization plot* allows the identification of all the LVMs, pseudo-LVMs[58] (pLVMs), and resonant modes associated with a defect. The marker method[59] is used to obtain the gap levels. The marker is the perfect crystal for all the defects, but we also use C_i as the marker for C3 and C4.

III. THREE WELL-KNOWN DEFECTS

A. Substitutional carbon: C_s

The carbon atom is at the substitutional site with tetrahedral symmetry. The four C-Si bond lengths are 2.01 Å. We find no gap level associated with C_s. The calculated and measured[1] triplet LVM of C_s and its isotopic shifts are given in Table I. The breathing mode of the four Si neighbors is at 459 cm^{-1} (below the Γ phonon). This mode drops to 451 cm^{-1} in ^{29}Si.

B. Interstitial carbon: C_i

In agreement with other authors,[26,27] we find that C_i has a split-⟨100⟩ configuration in the −, 0, and + charge states. In C_i^0, the C-Si bond lengths are 1.76 and 1.81 Å compared to 1.73 and 1.82 Å in Ref. 26 and 1.77 and 1.80 Å in Ref. 60. Using the perfect crystal as a marker, we find a donor and an acceptor level at $E_v+0.22$ eV and $E_c-0.11$ eV, respectively, very close to the measured[22,24,25] values $E_v+0.28$ eV and $E_c-0.10$ eV, respectively.

The calculated and measured[9,21,23] LVMs of C_i and its isotopic shifts (all in the neutral charge state) are given in Table II. Our calculated LVMs are very close to those calculated by other groups.[26,27]

TABLE I. Measured (Ref. 1) and calculated triplet LVM of ^{28}Si^{12}C (first line) and its isotopic shifts (in cm^{-1}).

	Expt.	This work
^{28}Si^{12}C	607.5	602
^{28}Si^{13}C	−18.4	−18
^{28}Si^{14}C	−34.7	−34
^{29}Si^{12}C	−3.5	−3

C. C3: C_iO_i

The C3 defect consists of a ring in the {01−1} plane, with threefold coordinated C and O atoms, a structure consistent with that reported by other authors.[34,37,38] The structures of C_i and C_iO_i are compared in Fig. 1. The three O-Si bond lengths are 1.8, 1.8, and 1.9 Å, respectively, and the three C-Si bond lengths are 1.8, 1.8, and 1.7 Å, respectively. We find no metastable or precursor structure to the C3 defect.

Our binding energies relative to the dissociated species in the 0 and + charge states are consistent with those of other authors,[34,38]

$$C_i^0 + O_i^0 \rightarrow C_iO_i^0 + 1.64 \text{ eV},$$

and

$$C_i^+ + O_i^0 \rightarrow C_iO_i^+ + 1.72 \text{ eV}.$$

Using the perfect crystal or C_i as a marker, C_iO_i has a donor level at $E_v+0.30$ eV or $E_v+0.37$ eV, respectively. The measured[35] value is $E_v+0.38$ eV. There is no acceptor level.

The localized vibrational modes (LVMs) and the various isotope combinations of the C_iO_i defect in the 0 and + charge states are shown in Fig. 2 and Table III. The calculated fre-

TABLE II. Measured (Refs. 9, 21, and 23) and calculated LVMs and isotopic shifts of C_i (in cm^{-1}).

	Expt.	This work
^{28}Si^{12}C	932.3	969
	922.3	901
^{28}Si^{13}C	–	−31
	–	−26
^{30}Si^{12}C	−7.9	−6
	−5.5	−8
^{30}Si^{13}C	−28.3	−37
	−30.3	−34

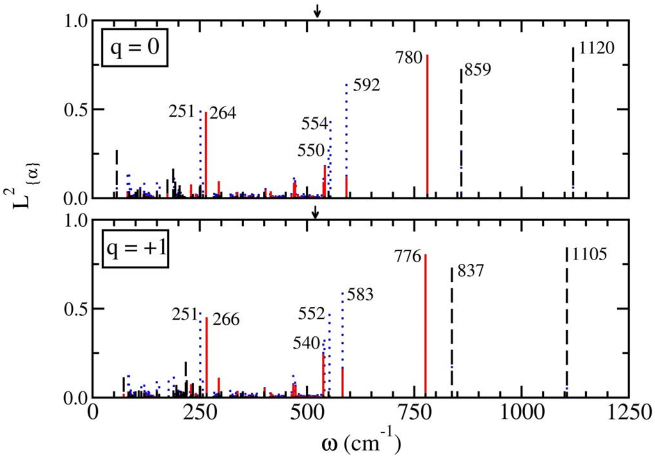

FIG. 2. (Color online) Vibrational spectra of the C3 defect in the 0 and + charge states for the ^{28}Si, ^{12}C, and ^{16}O isotopes. The lines are the calculated oscillation amplitudes not IR intensities (see Sec. II). They show on which atom a given LVM is localized. The dashed (black) lines correspond to C, the solid (red) lines to O, and the dotted (blue) lines to the Si neighbor. The arrow shows the calculated Γ phonon.

quencies and their isotope shifts compare well with the measured[12,21] values.

In the 0 charge state and for the ^{28}Si, ^{12}C, and ^{16}O isotopes, Fig. 2 shows the two mostly C-related modes at 1120 and 859 cm^{-1} (measured: 1116.3 and 865.9 cm^{-1}, respectively). The O-related modes are at 780 cm^{-1} (measured: 742.8 cm^{-1}) and 550 cm^{-1} (measured: 550 or 546 cm^{-1}). Two modes at 592 and 554 cm^{-1} are associated with the Si nearest neighbors to C and O (measured: 588 and either 550 or 546 cm^{-1}, respectively). Note the two pLVMs at 264 (O related) and 251 cm^{-1} (Si related).

TABLE III. Measured (Refs. 12 and 21) and calculated LVMS and isotopic shifts of C_iO_i in cm^{-1} in the 0 charge state. The isotope shifts in the + charge state are very close to the ones listed here.

	Expt.	This work
^{12}C^{16}O	1116.3	1120
	865.9	859
	742.8	780
	588	592
	550	554
	546	550
		264
^{13}C^{16}O	−36.4	−36
	−23.9	−24
	0.5	−1
		0
	0.2	0
	0.5	0
		0
^{12}C^{18}O	1.0	−1
	0.15	0
	33.4	−35
	3	−3
	0.3	0
	1.5	0
		−7

IV. C4: $Si_iC_iO_i$

All of the geometry optimizations converge toward one of three configurations of C4 (Fig. 3), labeled C4(a), C4(b), and C4(c). The (a) structure was studied by Backlund;[19] (b) and (c) structures were considered by Coutinho.[21,61] These defects have C_1 symmetry and all of the LVMs are IR active, but some IR intensities could be very small.

All three configurations have a donor level in the gap. Using the perfect crystal as a marker, it is at $E_v+0.11$ eV, $E_v+0.24$ eV, and $E_v+0.74$ eV for C4(a), C4(b), and C4(c), respectively. Using C_i as a marker, it is at $E_v+0.17$ eV, $E_v+0.30$ eV, and $E_v+0.80$ eV, respectively. C4(a) and C4(b) have no other level in the gap, but C4(c) has an acceptor level at $E_c-0.12$ eV or $E_c-0.11$ eV using the perfect crystal or C_i as a marker, respectively.

A. 0 charge state

In the 0 charge state, the lowest energy configuration is C4(a). It consists of a ring in the $\{01-1\}$ plane similar to the C3 defect but with the addition of Si_i on the carbon side of the ring. Thus, C4(a) is characterized by a threefold coordinated O atom, which suggests low-frequency LVMs. The four C-Si bond lengths are 1.84, 1.85, 1.89, and 1.89 Å, respectively, and the three O-Si bond lengths are 1.77, 1.81, and 1.84 Å, respectively. The binding energy of $Si_iC_iO_i^0$ relative to isolated Si_i and $C_iO_i^0$ is 1.50 eV; relative to O_i and $Si_iC_i^0$, it is 1.57 eV. Although these binding energies are smaller than those of C_iO_i (1.64 and 1.72 eV in the 0 and + charge states, respectively), they are on the high side since C_iO_i and $Si_iC_iO_i^0$ anneal out in the range of 300−400 °C (Ref. 23) and 150−200 °C,[42] respectively.

The C4(b) structure is 0.27 eV higher than C4(a). The C, O, and their common Si neighbor are in the $\{01-1\}$ plane. The fourfold coordinated C atom has bond lengths of 1.84, 1.86, 1.89, and 1.89 Å, respectively. The two O-Si bond lengths are 1.65 and 1.67 Å, respectively. In contrast to C4(a), one expects to find a high-frequency LVM associated with the twofold coordinated O atom, as predicted by Coutinho.[21]

The C4(c) structure is 0.39 eV higher than C4(a). Once again, this structure involves a ring containing C, O, and Si in the $\{01-1\}$ plane, but Si_i is near the hexagonal interstitial site nearest to the C atom. Carbon is fourfold coordinated with C-Si bond lengths of 1.84, 1.84, 1.85, and 1.94 Å, respectively. The threefold coordinated O atom has O-Si bond lengths of 1.77, 1.81, and 1.86 Å, respectively.

The vibrational spectra of the three structures for the ^{28}Si^{12}C^{16}O isotope combination are shown in Fig. 4 and tabulated in Table IV. Surprisingly, all three structures have LVMs that could be consistent with the observed[21,42,45]

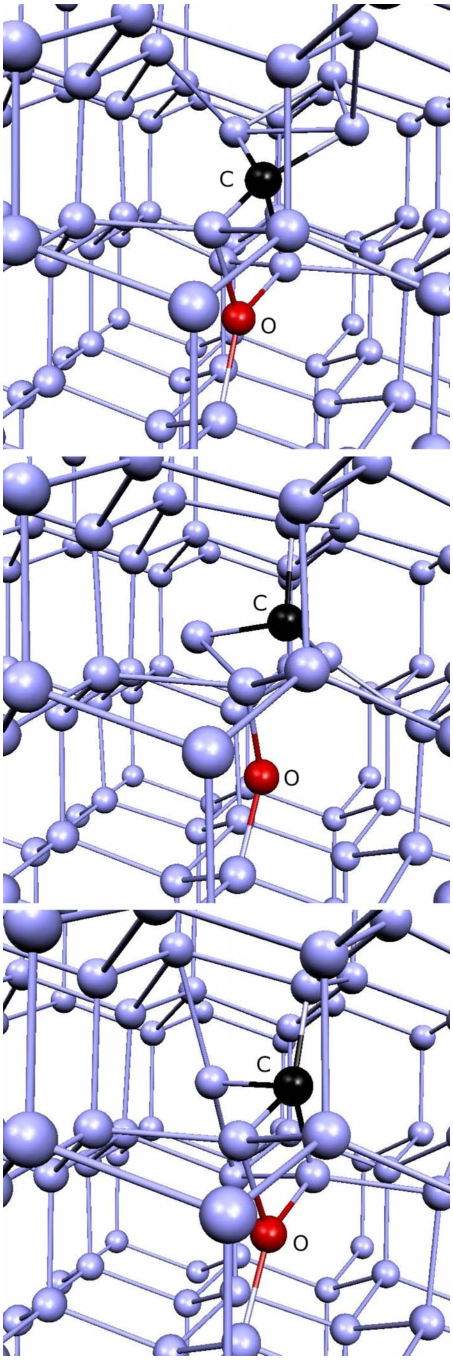

FIG. 3. (Color online) The three configurations of the C4 defect are labeled C4(a) (top), C4(b) (middle), and C4(c) (bottom), respectively. In the 0 charge state, the stable configuration is C4(a). In the + charge state, it is C4(c).

1024 cm^{-1} (O related) and 940 cm^{-1} (C related) ones, as well as the 760 cm^{-1} line that has recently been associated with the C4 defect (there have been no isotope-shift studies for it).

In the case of C4(a) and C4(c), the O-related 1024 cm^{-1} mode would be a 753+264=1017 or 763+265=1028 cm^{-1} combination mode, while the 760 cm^{-1} mode would be O related at 753 and 763 cm^{-1}, respectively. The C-related 940 cm^{-1} mode would be at 923 and 978 cm^{-1}, respectively.

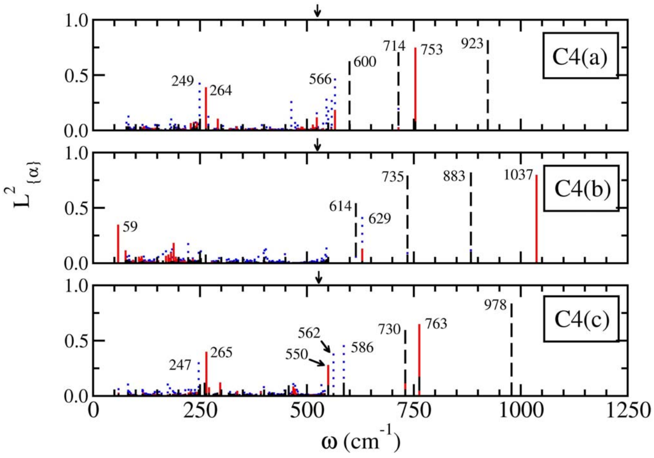

FIG. 4. (Color online) Vibrational spectra of the three configurations of the C4 defect in the 0 charge state for the ^{28}Si, ^{12}C, and ^{16}O isotope combinations. The lines are oscillation amplitudes, not IR intensities (Sec. II). The dashed (black) lines correspond to C, the solid (red) lines to O, and the dotted (blue) lines to the Si neighbor. The arrow shows the calculated Γ phonon.

In the case of C4(b), the O-related 1024 cm^{-1} mode would be at 1037 cm^{-1}. The C-related 940 cm^{-1} mode would be at 883 cm^{-1}. However, the 760 cm^{-1} mode would be C-related at 735. Note that the LVMs of C4(b) were calculated by Coutinho [21] to be at 998 cm^{-1} (our 1037 cm^{-1}), 908 cm^{-1} (our 883 cm^{-1}), 744 cm^{-1} (our 735 cm^{-1}), and 683 cm^{-1} (our 614 cm^{-1}).

Murin *et al.*[42] reported that following anneals near 200 and 275 °C, the 940 and 1024 cm^{-1} evolve into new lines,

TABLE IV. Measured (Refs. 21 and 42) and calculated LVMs and isotopic shifts of neutral $\text{Si}_i\text{C}_i\text{O}_i$ (Fig. 4). The correlation between the 760 cm^{-1} line and the C4 defect has only been reported by one group (Ref. 45). In the case of C4(a) and C4(c), the highest-frequency mode is a combination mode (the isotope shifts are the sum of the shifts of the two modes).

	Expt.	C4(a)	C4(b)	C4(c)
$^{28}\text{Si}^{12}\text{C}^{16}\text{O}$	1024.2	753+264	1037	763+265
	939.8	923	883	978
	760	714	735	730
		600	614	550
$^{28}\text{Si}^{13}\text{C}^{16}\text{O}$	−11.7	0	0	0
	−28.6	−29	−28	−26
		−19	−22	−19
		−14	−12	−12
$^{28}\text{Si}^{12}\text{C}^{18}\text{O}$	−41.9	−34	−48	−55
	−0.6	−3	0	−2
		−3	0	−2
		0	0	0
$^{30}\text{Si}^{12}\text{C}^{16}\text{O}$	−6.7	−4	−7	−11
	−6.6	−5	−5	−4
		−7	−5	−10
		−8	−9	−9

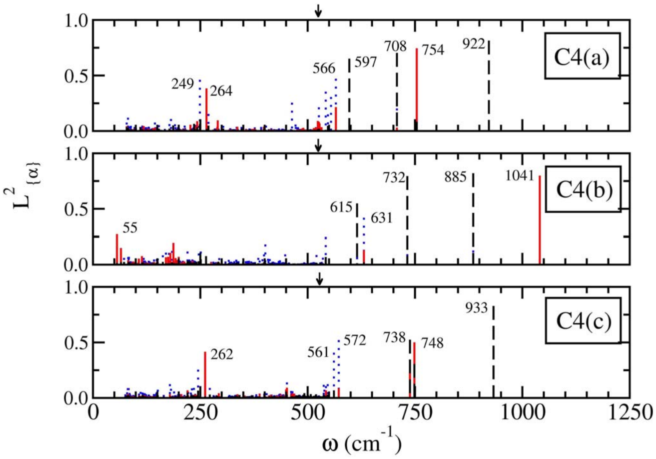

FIG. 5. (Color online) Vibrational spectra of the three configurations of the C4 defect in the + charge state for the ^{28}Si, ^{12}C, and ^{16}O isotopes. The lines are oscillation amplitudes, not IR intensities (Sec. II). The dashed (black) lines correspond to C, the solid (red) lines to O, and the dotted (blue) lines to the Si neighbor. The arrow shows the calculated Γ phonon.

which they believed to be related to different configurations of C4 and labeled as C4* and C4**. At 200 °C, the C4* lines are at 724 cm^{-1} (O related), 952 cm^{-1} (C related), and 973 cm^{-1} (C related). At 275 °C, the C4** lines are at 969 cm^{-1} (O related), 951 cm^{-1} (C related), and 977 cm^{-1} (C related). These combinations of modes are inconsistent with the vibrational spectra in Fig. 4.

B. + charge state

In the + charge state, the lowest energy configuration is C4(c). The C4(a) and C4(b) structures are 0.20 and 0.33 eV higher, respectively. The binding energy of $Si_iC_iO_i^+$ relative to isolated Si_i and $C_iO_i^+$ is 1.52 eV; relative to O_i and $Si_iC_i^+$, it is 1.65 eV. The vibrational spectra of the three structures for the ^{28}Si^{12}C^{16}O isotope combination are shown in Fig. 5. The frequency shifts relative to the 0 charge state are small.

V. DISCUSSION

We have calculated the structural, vibrational, and electrical properties of the C_s, C_i, C_iO_i, and $Si_iC_iO_i$ centers in Si. Our results for the first three centers closely reproduce the experimental data and confirm earlier theoretical predictions. The calculated properties of $Si_iC_iO_i$, i.e., the C4 defect, provide some insight into the (rather limited) amount of experimental information available.

We find three configurations for the C4 defect. The two metastable configurations are within 0.27 and 0.38 eV of the ground state, respectively. The binding energy of C4 ($\sim$1.50 eV) is smaller than that of C3 ($\sim$1.64 eV). These defects begin to anneal out at 150 and 300 °C, respectively. Note that the calculated binding energies are potential energy, not free energy, differences. The latter are smaller.[62]

The C4 structures have a donor level in the gap. Using the C_i as a marker, the donor level of C4(a), C4(b), and C4(c) is at $E_v+0.17$ eV, $E_v+0.30$ eV, and $E_v+0.80$ eV, respectively, close to the values we obtain with the perfect crystal as a marker. C4(c) has an acceptor level at $E_{c-0.11}$ eV. No electrical activity has been reported for this center.

The vibrational spectra of all three configurations could produce the measured 940 (C related) and 1024 cm^{-1} (O related) IR lines as well as the 760 cm^{-1} line. However, the latter line would be associated with O in the case of C4(a) and C4(c) and with C in the case of C4(b). The isotope shifts of this line have not yet been measured. The calculated isotope shifts of the 940 and 1024 cm^{-1} lines are compared to experiment in Table IV. Again, all three configurations could, in principle, correspond to the measured defect.

None of the three configurations of C4 has LVMs consistent with the C4* and C4** defects proposed by Murin *et al.*[42] in their annealing experiments. Indeed, C4* would have an O-related LVM 724 cm^{-1} and two C-related LVMs at 952 and 973 cm^{-1}. As shown in Fig. 4, none of our C4 structures has such a combination of modes. As for C4**, it would have an O-related LVM at 969 cm^{-1} and two C-related LVMs at 951 and 977 cm^{-1}. Again, we find no such combination of modes. We note that Londos[45] suggested that these new modes could result not from metastable configurations of C4 but from the formation of new defects, for example $Si_{n>1}C_iO_i$.

In conclusion, our results suggest the possible experiments. First, the association of the 760 cm^{-1} mode with C4 needs to be confirmed. Second, isotopic studies on that line would establish if it is O related, as in C4(a) and C4(c), or C-related, as in C4(b). Third, we predict that all the structures of C4 have a deep donor level in the gap. Although DLTS studies are difficult to perform in heavily irradiated samples, PL studies could be successful. Fourth, the conflicting results of two independent annealing studies[42,44] show that the evolution this defect is far from understood and may depend on the history of the sample. We find three possible configurations for C4 but none of them exhibits LVMs consistent with the suggested C4* and C4** defects.

ACKNOWLEDGMENTS

The authors are grateful to G. Davies, J. Coutinho, and C.A. Londos for valuable discussions. The work of SKE is supported in part by the Silicon Solar Consortium and Grant No. D-1126 from the R. A. Welch Foundation. Many thanks to Texas Tech's High Performance Computer Center for generous amounts of computer time.

*stefan.estreicher@ttu.edu

[1] G. Davies and R. C. Newman, in *Handbook on Semiconductors*, edited by S. Mahajan (Elsevier, Amsterdam, 1994), Vol. 3, p. 1557.
[2] B. Pajot, in *Oxygen in Silicon*, Semiconductors and Semimetals Vol. 42, edited by F. Shimura (Academic, Boston, 1994), p. 191.
[3] R. C. Newman and J. Wakefield, J. Phys. Chem. Solids **19**, 230 (1961).
[4] L. J. Cheng and P. Vajda, J. Appl. Phys. **40**, 4679 (1969).
[5] G. Davies, E. C. Lightowlers, E. C. Wooley, R. C. Newman, and A. S. Oates, J. Phys. C **17**, L499 (1984).
[6] S. Zhao, A. M. Agarwal, J. L. Benton, G. H. Gilmer, and L. C. Kimerling, in *Defects in Electronic Materials II*, MRS Symposia Proceedings No. 442, edited by J. Michel, T. Kennedy, K. Wada, and K. Thonke (Materials Research Society, Pittsburgh, 1997), p. 231.
[7] G. D. Watkins and K. L. Brower, Phys. Rev. Lett. **36**, 1329 (1976).
[8] P. Werner, H.-J. Gossmann, D. C. Jacobson, and U. Gösele, Appl. Phys. Lett. **73**, 2465 (1998).
[9] A. R. Bean and R. C. Newman, Solid State Commun. **8**, 175 (1970).
[10] L. W. Song, X. D. Zhan, B. W. Benson, and G. D. Watkins, Phys. Rev. Lett. **60**, 460 (1988); Phys. Rev. B **42**, 5765 (1990).
[11] E. V. Lavrov, L. Hoffmann, and B. B. Nielsen, Phys. Rev. B **60**, 8081 (1999).
[12] G. Davies, A. S. Oates, R. C. Newman, R. Wooley, E. C. Lightowlers, M. J. Binns, and J. G. Wilkes, J. Phys. C **19**, 841 (1986).
[13] J. M. Trombetta and G. D. Watkins, Appl. Phys. Lett. **51**, 1103 (1987).
[14] M. R. Brozel, R. C. Newman, and D. H. J. Totterdell, J. Phys. C **8**, 243 (1975).
[15] G. Davies, E. C. Lightowlers, R. C. Newman, and A. S. Oates, Semicond. Sci. Technol. **2**, 524 (1987).
[16] M. S. Potsidi and C. A. Londos, J. Appl. Phys. **100**, 033523 (2006).
[17] C. A. Londos, M. S. Potsidi, G. D. Antonaras, and A. Adrianakis, Physica B **367**, 165 (2006).
[18] A. Mattoni, F. Bernardini, and L. Colombo, Phys. Rev. B **66**, 195214 (2002).
[19] D. J. Backlund and S. K. Estreicher, Physica B (Amsterdam) **401-402**, 163 (2007).
[20] R. C. Newman and J. B. Willis, J. Phys. Chem. Solids **26**, 373 (1965).
[21] G. Davies, S. Hayama, S. Hao, B. B. Nielsen, J. Coutinho, M. Sanati, S. K. Estreicher, and K. M. Itoh, Phys. Rev. B **71**, 115212 (2005).
[22] L. W. Song and G. D. Watkins, Phys. Rev. B **42**, 5759 (1990).
[23] L. I. Murin, V. P. Markevich, J. L. Lindström M. Kleverman, J. Hermansson, T. Hallberg, and B. G. Svensson, Solid State Phenom. **82-84**, 57 (2002).
[24] L. C. Kimerling, P. Blood, and W. M. Gibson, in *Defects and Radiation Damage in Semiconductors 1978*, IOP Conference Proceedings No. 46 (The Institute of Physics, London and Bristol, 1979) p. 273.
[25] C. A. Londos, Phys. Rev. B **35**, 6295 (1987); Semicond. Sci. Technol. **5**, 645 (1990).
[26] P. Leary, R. Jones, S. Öberg, and V. J. B. Torres, Phys. Rev. B **55**, 2188 (1997).
[27] R. Jones, B. J. Coomer, and P. R. Briddon, J. Phys.: Condens. Matter **16**, S2643 (2004).
[28] A. V. Yukhnevich, V. D. Tkachev, and M. V. Bortnik, Sov. Phys. Solid State **8**, 1004 (1966).
[29] G. Davies, E. C. Lightowlers, and M. do Carmo, J. Phys. C **16**, 5503 (1983).
[30] K. Thonke, G. D. Watkins, and R. Sauer, Solid State Commun. **51**, 127 (1984).
[31] W. Kürner, R. Sauer, A. Dörnen, and K. Thonke, Phys. Rev. B **39**, 13327 (1989).
[32] E. C. Lightowlers and A. N. Safonov, Mater. Sci. Forum **258-263**, 617 (1997).
[33] N. Inoue, Y. Goto, and T. Sugiyama, Solid State Phenom. **131-133**, 207 (2008).
[34] J. Coutinho, R. Jones, P. R. Briddon, S. Öberg, L. I. Murin, V. P. Markevich, and J. L. Lindström, Phys. Rev. B **65**, 014109 (2001).
[35] P. M. Mooney, L. J. Cheng, M. Süli, J. D. Gerson, and J. W. Corbett, Phys. Rev. B **15**, 3836 (1977).
[36] K. Shinoda and E. Ohta, Appl. Phys. Lett. **61**, 2691 (1992).
[37] R. Jones and S. Öberg, Phys. Rev. Lett. **68**, 86 (1992).
[38] S. Hao, L. Kantorovich, and G. Davies, J. Phys.: Condens. Matter **16**, 8545 (2004).
[39] S. Hayama, G. Davies, J. Tan, J. Coutinho, R. Jones, and K. M. Itoh, Phys. Rev. B **70**, 035202 (2004).
[40] A. S. Oates, M. J. Binns, R. C. Newman, J. H. Tucker, J. C. Wilkes, and A. Wilkinson, J. Phys. C **17**, 5695 (1984).
[41] A. S. Oates and R. C. Newman, Appl. Phys. Lett. **49**, 262 (1986).
[42] L. I. Murin, J. L. Lindström, G. Davies, and V. P. Markevich, Nucl. Instrum. Methods Phys. Res. B **253**, 210 (2006).
[43] V. P. Markevich (private communication).
[44] C. A. Londos, M. S. Potsidi, and E. Stakakis, Physica B (Amsterdam) **340-342**, 551 (2003).
[45] C. A. Londos (private communication).
[46] Y. H. Lee, Appl. Phys. Lett. **73**, 1119 (1998).
[47] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).
[48] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J. M. Soler, Phys. Status Solidi B **215**, 809 (1999).
[49] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[50] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[51] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[52] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[53] S. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[54] O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989); O. F. Sankey, D. J. Niklewski, D. A. Drabold, and J. D. Dow, *ibid.* **41**, 12750 (1990).
[55] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).
[56] X. Gonze, Phys. Rev. A **52**, 1096 (1995); X. Gonze and C. Lee, Phys. Rev. B **55**, 10355 (1997).
[57] J. M. Pruneda, S. K. Estreicher, J. Junquera, J. Ferrer, and P. Ordejón, Phys. Rev. B **65**, 075210 (2002).

[58] S. K. Estreicher, D. West, J. Goss, S. Knack, and J. Weber, Phys. Rev. Lett. **90**, 035504 (2003); S. K. Estreicher, D. West, and M. Sanati, Phys. Rev. B **72**, 121201(R) (2005).

[59] J. P. Goss, M. J. Shaw, and P. R. Briddon, in *Theory of Defects in Semiconductors*, edited by D. A. Drabold and S. K. Estreicher (Springer, Heidelberg, 2007), p. 69.

[60] R. B. Capaz, A. Dal Pino, Jr., and J. D. Joannopoulos, Phys. Rev. B **50**, 7439 (1994).

[61] J. Coutinho (private communication).

[62] M. Sanati and S. K. Estreicher, Phys. Rev. B **72**, 165206 (2005).