Formation of interstitial carbon–interstitial oxygen complexes in silicon: Local vibrational mode spectroscopy and density functional theory

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Local vibrational mode (LVM) spectroscopy has been used to investigate the evolution of complexes related to interstitial carbon (C_i) atoms in low-temperature-irradiated silicon crystals containing different carbon and oxygen isotopes. It is found that in oxygen-rich Si crystals in the course of the formation of the stable interstitial carbon–interstitial oxygen defect (C_iO_i), three metastable complexes incorporating C_i and O_i atoms occur. Local vibrational modes for all these defects with different combinations of carbon and oxygen isotopes are determined. Density functional modeling studies have been used to investigate the structural, electronic, and vibrational properties of several C_iO_i complexes. In addition to the most stable C_iO_i center, other stable structures incorporating C_i and O_i atoms have been found which account well for the LVM spectroscopy and deep-level transient spectroscopy data.

I. INTRODUCTION

Oxygen and carbon are important technological impurities in silicon.[1,2] In as-grown Si crystals these impurities are present mainly as isolated atoms located at interstitial-bond-centered (Si-O_i-Si) and substitutional (C_s) sites, respectively. Single O_i and C_s atoms are electrically inactive. However, the presence of oxygen and carbon impurities can cause significant changes in electrical properties of Si crystals upon various technological treatments since in crystals subjected to different radiation and/or thermal treatments these impurities interact with themselves and other lattice defects to form a variety of electrically active complexes. Substitutional carbon atoms are known to be effective traps for silicon self-interstitials.[2–4] Interstitial carbon atoms (C_i) formed via the Watkins replacement mechanism are mobile at $T \geq 270$ K and can interact effectively with other impurities and defects.[2,5–7]

In Si crystals grown by the Czochralski technique (Cz-Si), interstitial oxygen atoms are among the dominant traps for mobile C_i.[5,8,9] Resulting interstitial carbon–interstitial oxygen complex (C_i-O_i) is one of the main radiation-induced defects in irradiated Cz-Si crystals. This defect was observed and identified with the use of various experimental techniques: (i) infrared (IR)–absorption spectroscopy [the most intense local vibrational mode (LVM) lines at 865 and 1116 cm^{-1}],[6,10–13] (ii) photoluminescence (C line with $h\nu$ = 790 meV),[11,14] (iii) electron-spin resonance (Si-G15 signal),[15] and (iv) Hall effect and deep-level transient spectroscopy (DLTS) (an energy level at about E_V+0.36 eV).[5,16]

On the basis of an analysis of the available experimental results and *ab initio* modeling, a structural model of the C_iO_i complex has been proposed.[12,13,17] According to this model, oxygen and carbon atoms do not form direct bonds with each other and its local vibrational modes can be separated into "oxygen related" and "carbon related." The oxygen atom in the C_iO_i complex is threefold coordinated and gives rise to an absorption band at about 740 cm^{-1}, which is only slightly sensitive to isotope substitution of the carbon atom.[6,12,13,17] The two most intense absorption lines at 865 and 1116 cm^{-1} are associated with vibrations localized on the carbon atom. A ^{16}O to ^{18}O isotope substitution does not result in significant changes in the wavelength of these modes. The configuration of carbon in the complex is similar to that for the single C_i impurity in Si,[13,15] and therefore it is the main source of electrical activity of the C_iO_i complex.

Meanwhile, in spite of numerous studies of the C_iO_i complex, some questions related to the mechanism of its formation are still unanswered. Obviously, the defect is formed when a mobile C_i atom is localized near an interstitial oxygen atom. However, before the formation of the most stable configuration of the center, some intermediate metastable configurations appear to be formed. In silicon such metastable defects are known to precede the formation of stable vacancy-oxygen and C_iC_s complexes.[18–20] The existence of such precursors for the C_iO_i complex was evidenced in DLTS and IR-absorption measurements.[10,21–27] It was reported in Ref. 21 that the disappearance of the C_i defect in n-type Cz-Si crystals irradiated with α particles resulted in the formation of a metastable C_iO_i precursor with an energy

level at $E_V+0.38$ eV, which subsequently transformed to a stable configuration with an energy level at $E_V+0.35$ eV. References 22 and 23 also reported the simultaneous appearance of two defects with similar energy levels at $E_V+0.35$ eV and at $E_V+0.38$ eV upon annealing of the C_i center. The defect with a level at $E_V+0.35$ eV was unstable at room temperature (RT) and its disappearance was accompanied by further growth in concentration of the stable C_iO_i center with an energy level at $E_V+0.38$ eV. Moreover, annealing and DLTS measurements on electron-irradiated phosphorus-doped Cz-Si link an additional level at $E_C-0.06$ eV to a precursor of C_iO_i.[27] It was suggested on the basis of these observations that the stable configuration of the C_iO_i complex can be formed in two ways, either: (a) through a direct capture of an interstitial carbon atom by an oxygen atom (this process is limited only by diffusion of C_i) or (b) through an intermediate metastable configuration, referred as the M center in Ref. 22, which is separated from the most stable configuration by an energy barrier that is higher than the activation energy of C_i diffusion.

The existence of an intermediate stage or delay between the disappearance of the C_i complex and appearance of the bands at 865 and 1115 cm^{-1}, which are related to the stable C_iO_i complex, was mentioned previously in the study of transformations of carbon-related complexes in irradiated Cz-Si crystals by means of IR absorption.[10,24] However, no absorption bands, which could be associated with the complexes formed during the intermediate stage, were reported. Such bands were observed first in Ref. 25, where some of the bands detected in irradiated and annealed Cz-Si crystals were tentatively assigned to a precursor of the C_iO_i complex. The most intense line among the new bands was at 967 cm^{-1}. Further support for this suggestion was found recently in Ref. 26, where a few additional lines associated with C_iO_i precursors were reported. The existence of such centers was confirmed by DLTS.

Here we report results of a detailed IR-absorption study of annealing out of the C_i center and the formation of C_iO_i complexes in Si crystals doped with different oxygen and carbon isotopes. We also report a density functional modeling study in order to investigate the structural, electronic, and vibrational properties of several metastable C_iO_i complexes. In addition to the most stable C_iO_i center, we report on another stable structure incorporating C_i and O_i atoms that accounts well for the IR-absorption and DLTS data.

II. EXPERIMENTAL DETAILS

Three types of Si:O,C samples were used. The first one (1) contained ^{12}C and ^{16}O, while the second (2) contained mainly ^{13}C and ^{16}O. ^{12}C and ^{13}C atoms were introduced into the crystals when they were grown by the Czochralski technique from melts into which precise amounts of carbon isotope powders were added. The third (3) sample was doped with ^{12}C and a mixture of ^{16}O and ^{18}O isotopes. The ^{18}O-enriched crystal was grown by float-zone regrowth of a Cz-Si rod under an ambient containing a defined partial pressure of ^{18}O. Carbon and oxygen concentrations in sample 1 were 6.35×10^{17} and 9.3×10^{17} cm^{-3}, respectively. In

sample 2 the concentrations of $^{12}C_s$, $^{13}C_s$, and $^{16}O_i$ were 3.0×10^{16}, 1.2×10^{17}, and 1.0×10^{18} cm^{-3}, respectively, while sample 3 contained about 3.06×10^{17} cm^{-3} of $^{12}C_s$, 1.04×10^{18} cm^{-3} of $^{16}O_i$, and 9.9×10^{17} cm^{-3} of $^{18}O_i$. The concentrations of oxygen and carbon were monitored by measuring the room-temperature intensities of the absorption bands at 1107 ($^{16}O_i$), 1058 ($^{18}O_i$), 605 ($^{12}C_s$), and 587 cm^{-1} ($^{13}C_s$).[2,28]

Vacancy- and self-interstitial-related intrinsic point defects were introduced into the samples by irradiation with 5 MeV electrons using a Microtron M30 accelerator. The temperature of the samples during irradiation was about 80 K. After irradiation the samples were transferred into a cryostat for optical measurements without heating. The low-temperature irradiation provided an opportunity to study defect-impurity interactions in the samples starting from the simplest ones and going to more complex cases with the increase in annealing temperature. The IR-absorption analysis was carried out using a Bruker 113v Fourier transform IR spectrometer. The measurements were performed at about 10 K and at RT with spectral resolutions of 0.5 and 1.0 cm^{-1}, respectively. Transformations of the C_i-related centers were studied upon isochronal annealing of the irradiated samples with temperature increments of 5–10 K in the range of 80–360 K, for 20 min at each temperature, in a special cryostat system.

III. EXPERIMENTAL RESULTS

Figure 1 shows difference absorption spectra measured at 10 K for a Si:^{12}C+^{16}O sample irradiated at 80 K and isochronally annealed up to 250, 290, 305, and 340 K. The absorption spectrum of a nonirradiated high-purity float-zone-grown Si sample was used as a reference for all the spectra shown. The most intense lines in the spectrum measured after annealing at 250 K [spectrum (a)] are at 835, 922.1, and 932.1 cm^{-1}. These lines arise from well-known local vibrational modes due to the vacancy-oxygen center and interstitial carbon.[1,2,29] Two weak lines at 960 and 966 cm^{-1} are most likely related to a complex which incorporates carbon and silicon interstitial atoms (C_iI_{Si}).[2,30] Anneals in the temperatures range from 260 to 340 K resulted in a gradual decrease in intensities of the C_i-related lines and to the appearance and development of a number of absorption lines. The most intense among them are at 865.9, 967.4, 1059.6, 1086.2, and 1116.3 cm^{-1}. The lines at 865.9 and 1116.3 cm^{-1} are well-known LVMs due to the stable configuration of the C_iO_i complex.[2,13] The lines at 967.4, 1059.6, and 1086.2 cm^{-1} together with a number of weaker lines disappeared from the spectra after anneals in the temperature range of 290–340 K. An analysis of changes in line intensities upon isochronal annealing in the temperature range of 260–340 K allows us to separate the unstable lines into three groups on the basis of their annealing behaviors. The lines from the first and the second groups developed in the temperature range of 260–305 K, while the lines from the third group were seen in the spectra after anneals in the temperature range of 270–340 K. Figures 2(a) and 3(a) show developments of intensities of the lines from the first and the
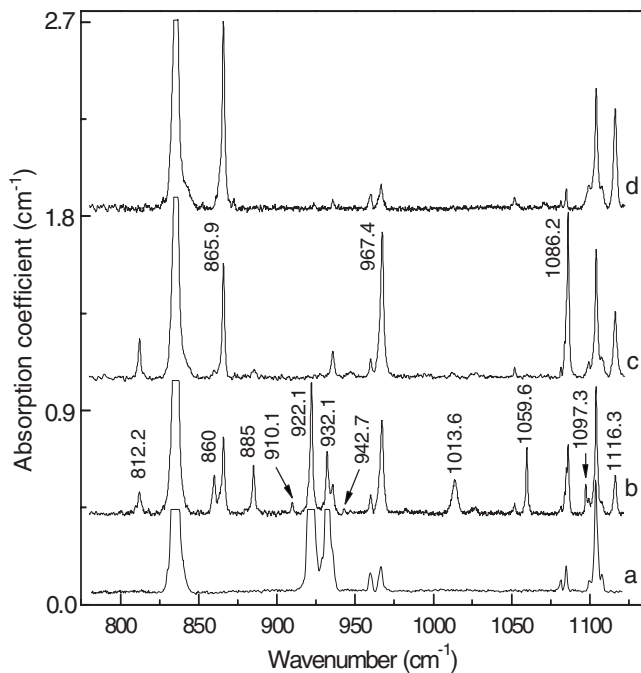
FIG. 1. Sections of absorption spectra measured at 10 K for a Si:^{12}C+^{16}O sample which was irradiated at 80 K with 5 MeV electrons and subjected to isochronal annealing with the last steps at (a) 250, (b) 290, (c) 305, and (d) 340 K. Irradiation dose was F =9×10^{17} cm^{-2}. Concentrations of interstitial oxygen and substitutional carbon atoms in the untreated sample were [^{16}O$_i$]=9.3 ×10^{17} cm^{-3} and [^{12}C$_s$]=6.35×10^{17} cm^{-3}. An absorption signal from a nonirradiated high-purity float-zone-grown Si sample was subtracted from each spectrum. The spectra are shifted on the vertical axis for clarity.
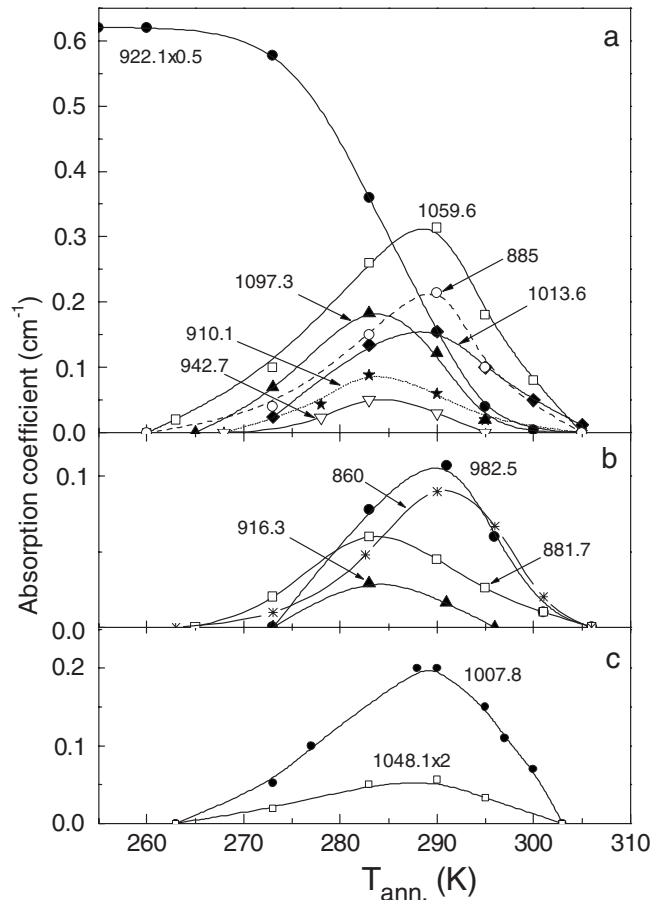

FIG. 2. Changes in intensities of absorption lines associated with interstitial carbon-related defects upon 20 min isochronal annealing of irradiated Si samples doped with different carbon and oxygen isotopes: (a) Si:^{12}C+^{16}O, (b) Si:^{12}C+^{13}C+^{16}O, and (c) Si:^{12}C+^{16}O+^{18}O. The absorption spectra of the samples are shown in Figs. 1, 4, and 5.

second groups and from the third group together with those of the lines due to the C$_i$ center and the C$_i$O$_i$ complex upon isochronal annealing.

The first group includes the lines at 910.1, 942.7, and 1097.3 cm^{-1}. The lines at 910.1 and 942.7 cm^{-1} were reported recently.[26] It was suggested that they are related to a precursor of the stable C$_i$O$_i$ complex.[26] The second group includes the lines at 885, 1013.6, and 1059.6 cm^{-1}. These lines have not been reported earlier.

It should be mentioned that a line at 860 cm^{-1} has developed in the spectra upon annealing in the same temperature range as the lines from the first and the second groups. This line was observed earlier in Ref. 20 and was assigned to a precursor of the stable C$_i$C$_s$ complex.

The third group of lines includes the lines at 812.2, 967.4, and 1086.2 cm^{-1}. Maximum intensities of the lines at 967.4 and 1086.2 cm^{-1} are much stronger than those of the lines from the first and the second groups. All the lines from the third group were observed earlier in Ref. 26 and were tentatively assigned to another precursor of the stable C$_i$O$_i$ complex.[26]

The presence of carbon and oxygen atoms in the complexes, which give rise to the LVM lines from all three groups, is demonstrated by observations of frequency shifts of their LVMs after replacement of ^{12}C and ^{16}O atoms by their isotopes. Figures 4 and 5 show infrared-absorption

spectra for irradiated and annealed Si samples enriched with ^{13}C and ^{18}O isotopes, respectively.

Earlier studies of a number of complexes incorporating C$_i$ and O$_i$ atoms in Si showed that carbon and oxygen atoms in those defects do not form direct covalent bonds.[2,12,13] So, as the C$_i$ and O$_i$ atoms are well separated, LVMs of the complexes can be divided into carbon-related and oxygen-related ones.[2,12,13] Frequencies of carbon-related LVMs are sensitive to isotope substitutions of C atoms but are practically insensitive to isotope substitutions of oxygen atoms, while the oxygen-related LVMs are sensitive only to isotope substitutions of O atoms. An analysis of isotope shifts and annealing behaviors (Figs. 2 and 3) of the lines in ^{13}C- and ^{18}O-doped Si samples allows us to find isotope counterparts for nearly all the lines mentioned above and assigned to vibrations of carbon or oxygen atoms. The results of the analysis together with suggested assignments of the lines are given in Table I.

It is found that the lines at 910.1 and 942.7 cm^{-1} from the first group are related to vibrations of carbon atoms, and the line at 1097.3 cm^{-1} is an oxygen-related LVM. Annealing behaviors of the two carbon-related lines from the first group are very similar to that of the line at 1097.3 cm^{-1}. We suggest that the line at 1097.3 cm^{-1} together with the carbon-
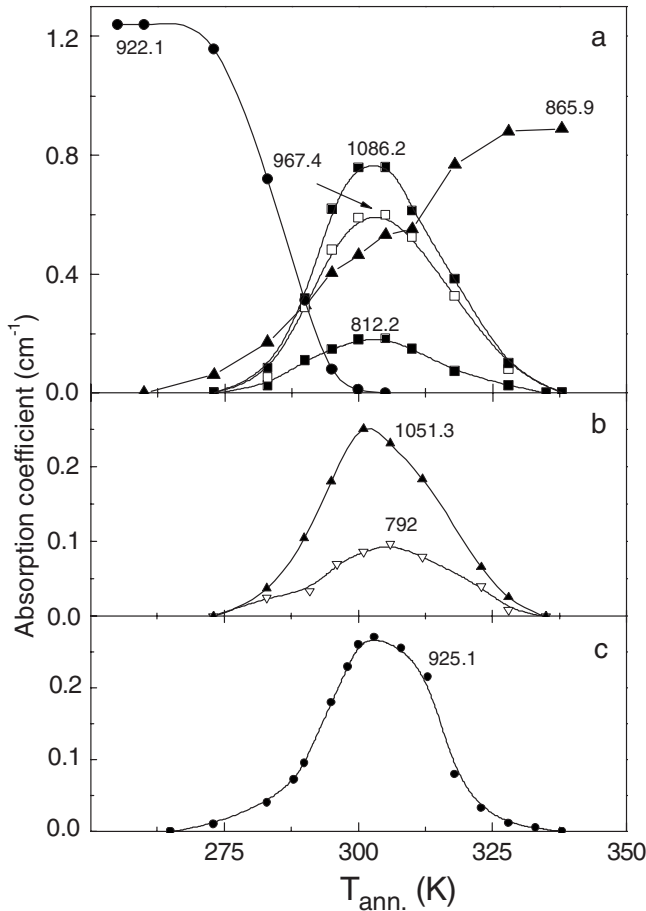
FIG. 3. Changes in intensities of absorption lines associated with interstitial carbon-related defects upon 20 min isochronal annealing of irradiated Si samples doped with different carbon and oxygen isotopes: (a) Si:^{12}C+^{16}O, (b) Si:^{12}C+^{13}C+^{16}O, and (c) Si:^{12}C+^{16}O+^{18}O. The absorption spectra of the samples are shown in Figs. 1, 4, and 5.

related lines at 910.1 and 942.7 cm^{-1} is related to a precursor of the stable C_iO_i complex. This precursor is labeled as C_i-O_i' in Table I.

Two lines at 885 and 1013.6 cm^{-1} from the second group are carbon-related LVMs, while the line at 1059.6 cm^{-1} is oxygen related. A line at 1007.8 cm^{-1} is suggested to be an ^{18}O-related isotope analog of the line at 1059.6 cm^{-1}. It should be mentioned, however, that in this case the isotope shift of the 1059.6 cm^{-1} line induced by replacement of ^{16}O atoms by ^{18}O isotopes is rather large, 51.8 cm^{-1}. This is nearly the same as that for the single interstitial oxygen atom in Si. It might be possible that the line at 1013.6 cm^{-1} in the ^{18}O-doped sample is a superposition of two lines, one of them being a carbon-related LVM, and the other being an ^{18}O-related isotope analog of the line at 1059.6 cm^{-1}. Line positions and values of the isotopes shifts observed for the lines from the second group are characteristic of threefold-coordinated C_i atoms and twofold-coordinated oxygen atoms incorporated into radiation-induced defects.[2,6] So, it is likely that the lines at 885, 1013.6, and 1059.6 cm^{-1} are associated with another precursor of the stable C_iO_i defect, and that precursor is labeled as C_i-O_i'' in Table I.
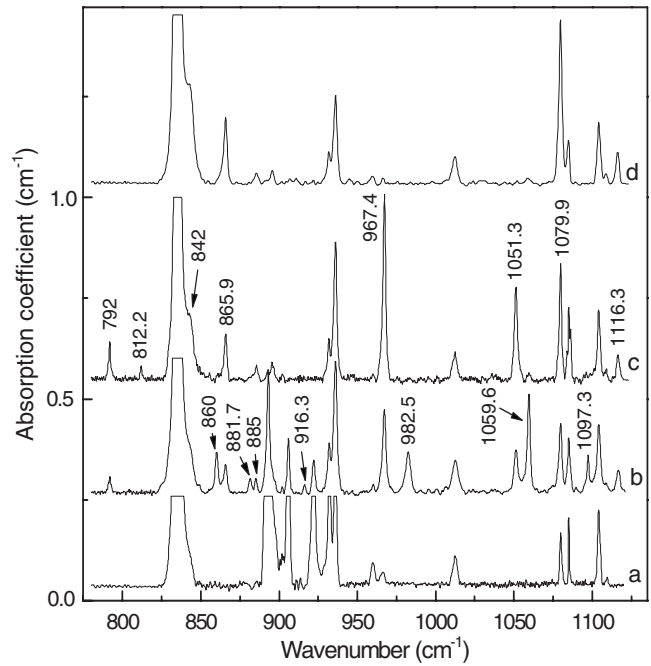

FIG. 4. Sections of absorption spectra measured at 10 K for a Si:^{12}C+^{13}C+^{16}O sample which was irradiated at 80 K with 5 MeV electrons and subjected to isochronal annealing with the last steps at (a) 250, (b) 290, (c) 305, and (d) 340 K. Irradiation dose was $F=9\times10^{17}$ cm^{-2}. Concentrations of interstitial oxygen and substitutional carbon atoms in the untreated sample were $[^{12}C_s]=3.0\times10^{16}$ cm^{-3}, $[^{13}C_s]=1.2\times10^{17}$ cm^{-3}, and $[^{16}O_i]=1.0\times10^{18}$ cm^{-3}. An absorption signal from a nonirradiated high-purity float-zone-grown Si sample was subtracted from each spectrum. The spectra are shifted on the vertical axis for clarity.

Isotope shifts of the lines from the third group show that two of them at 812.2 and 1086.2 cm^{-1} are carbon related and the line at 967.4 cm^{-1} is oxygen related (Table I). The disappearance of the lines from the second group is accompanied by a considerable increase in intensity of the bands related to C_iO_i (Fig. 3). The results of the present work confirm a suggestion, which was put forward in Ref. 26, that the lines at 812.2, 967.4, and 1086.2 cm^{-1} are related to the third precursor of the stable C_iO_i complex, C_i-O_i^*.

The results obtained indicate that at least three metastable C_i-O_i defects can be formed when a mobile interstitial carbon atom approaches an interstitial oxygen atom in Si lattice. An analysis of positions of carbon- and oxygen-related LVMs for all the precursors and the stable C_i and C_iO_i defects shows that there are certain trends in shifts of the LVMs of the complexes, which are formed on the way from C_i to the most stable C_iO_i defect.

For the first and the least stable defect, C_i-O_i', the LVMs at 910.1 and 942.7 cm^{-1} are very close to the LVMs of the single interstitial carbon atom at 922.1 and 932.1 cm^{-1}. Also the oxygen-related LVM of the C_i-O_i' at 1097.3 cm^{-1} is not far from the asymmetric stretching mode due to interstitial oxygen atom at 1136.4 cm^{-1}. So, it appears that the interstitial carbon atom is rather remote from an O_i atom in the C_i-O_i' and LVMs of the complex are associated with only slightly perturbed vibrations related to C_i and O_i atoms.
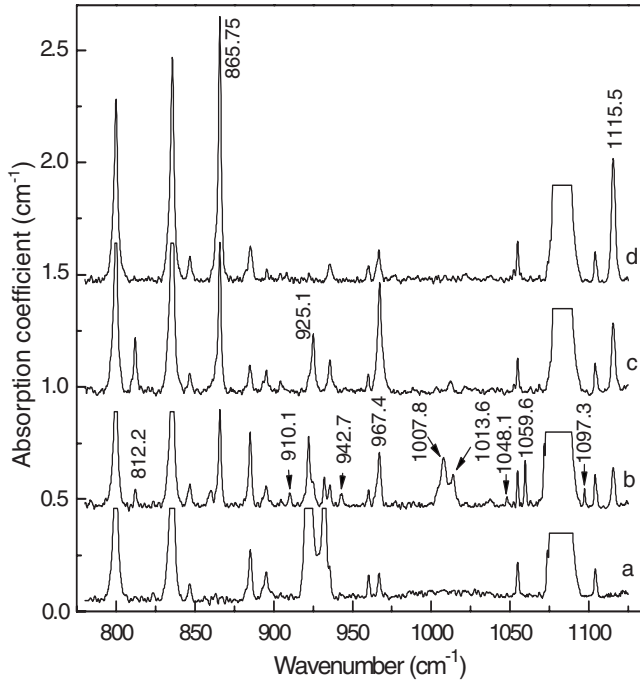
FIG. 5. Sections of absorption spectra measured at 10 K for a Si: ^{12}C + ^{16}O + ^{18}O sample which was irradiated at 80 K with 5 MeV electrons and subjected to isochronal annealing with the last steps at (a) 250, (b) 290, (c) 305, and (d) 340 K. Irradiation dose was F = 6×10^{17} cm^{-2}. Concentrations of interstitial oxygen and substitutional carbon atoms in the untreated sample were $[^{12}C_s]$ = 3.1×10^{17} cm^{-3}, $[^{16}O_i]$ = 1.04×10^{18} cm^{-3}, and $[^{18}O_i]$ = 9.9×10^{17} cm^{-3}. An absorption signal from a nonirradiated high-purity float-zone-grown Si sample was subtracted from each spectrum. The spectra are shifted on the vertical axis for clarity.

Further movement of a C_i atom toward an O_i atom results in the formation of another metastable complex, C_i-O_i'' with more strongly perturbed "C_i-" and "O_i-related" LVMs. Both carbon-related LVMs move further away from those due to a single C_i atom increasing the separation between the two modes; the oxygen-related LVM shifts to 1059.6 cm^{-1}.

It appears that in the C_i-O_i^* center C_i and O_i atoms are closer than in the first two metastable C_iO_i complexes. Carbon-related LVMs move further to 812.2 and 1086.2 cm^{-1}, and the high-frequency mode crosses with the oxygen-related LVM, which is at 967.4 for the C_i-O_i^*. As already mentioned, the maximum intensities of the LVMs due to C_i-O_i^* are stronger than those for the first metastable C_i-O_i centers, C_i-O_i' and C_i-O_i'', while the C_i-O_i^* complex is more stable than the first two defects. That is an indication that the binding energy of C_i-O_i complexes increases when a C_i atom moves closer to an interstitial oxygen atom.

For the most stable C_iO_i defect the high-frequency carbon-related LVM moves further to 1116.3 cm^{-1}, but the low-frequency LVM increases to 865.9 cm^{-1}. The oxygen atom becomes threefold coordinated and this results in the movement of the oxygen-related LVM down to 742.8 cm^{-1}.[12,13]

IV. THEORETICAL METHOD

We used a spin-density functional code [AIMPRO (Ref. 31)] together with a Padé form (Ref. 32) for the local-density approximation (LDA) to the exchange-correlation energy, using the parametrization by Perdew and Wang.[33] Core electrons are accounted for by using the pseudopotentials by Hartwigsen *et al.*,[34] whereas valence states are described with help of localized atomic *s*-, *p*-, and *d*-like Cartesian-Gaussian orbitals centered on every atom. Silicon, carbon, and oxygen atoms are assigned with (4,4,2), (4,4,2), and (4,4,4) basis sets, where the (n_s, n_p, n_d) triplets represent the number of *s*-, *p*-, and *d*-like sets of functions. These are made of 1, 3, and 6 functions, respectively, leading to a total of 28, 28, and 40 basis functions for each Si, C, and O atom, respectively. The charge density and potential energy are evaluated in reciprocal space. For that we limit the plane-wave kinetic energy at E_{cut} = 150 Ry. The electronic-structure calculations are coupled to an atomic-structure-relaxation procedure where all atoms are moved along the Hellmann-Feynman forces until their values become less than 0.02 eV/Å.

For most of the calculations, the crystalline host was modeled as a 64–Si atom cubic supercell, and its Brillouin zone was sampled at a total of 8 special **k** points from the MP-2^3 grid proposed by Monkhorst and Pack.[35] However, calculations where the O and C atoms are separated by more than one Si-Si bond were accomplished using 216–Si atom cubic supercells. As in previous reports we found that these conditions account well for converged total energies and vibrational modes.[13] We adopted the theoretical lattice parameter, a_0 = 5.395 Å, which compares well with 5.431 Å from x-ray measurements.[36] Local vibrational mode frequencies were calculated from *ab initio* second derivatives of the energy with respect to atomic displacement. These were obtained from the force derivatives after moving pairs of C, O, and neighboring Si atoms along all six Cartesian directions.

There are several ways to estimate electrical levels of defects within the gap. We single out two popular methods,[37] namely, the *formation-energy method* which is a first-principles approach, and the semiempirical *marker method*. The former method attempts to estimate the Fermi-level location of a defect ensemble where a charge-state transition takes place, whereas the latter compares electron affinities and ionization energies of a defect under scrutiny with the same quantities obtained for a well-characterized center (referred to as *marker* defect). The marker method works best when the electronic structure of the marker is similar in character, symmetry, extent, etc., to that of the defect being studied. We find these similarities between C_i, C_iO_i, and a metastable form of C_iO_i, referred as C_i-O_i^*, which are the source of interest in this work. Therefore, $C_i(-/0)$ = E_C - 0.10 eV and $C_i(0/+)$ = E_V + 0.28 eV levels were chosen to *mark* the calculations. Accordingly, a donor level of a defect D is given by

$$E_D(0/+) - E_V = I_D(0/+) - I_M(0/+) + [E_M(0/+) - E_V]_{expt},$$

where the subscripts D and M stand for defect and marker, respectively, $I_x(0/+) = E_x(0) - E_x(+)$, with $E_x(q)$ being the to-

TABLE I. Positions of local vibrational mode lines (in cm^{-1}) associated with interstitial carbon–related centers, which were observed in the Si samples studied, annealing temperature ranges in which the centers were detected, and suggested assignment of the lines. ND means "not detected." LVM frequencies for C_i, C_iO_i, and $C_iO_i^*$ centers calculated in the present work with the use of the AIMPRO package are also given.

| $^{12}C+^{16}O$ | | $^{13}C+^{16}O$ | | $^{12}C+^{18}O$ | | Temperature range of existence | Assignment |
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	(K)	
960		931.7		960		80–500	C_iSi_i [a]
966		936.4		966			
860		ND		860		270–310	$C_iC_S^*$ [b]
966		928		966			
922.1	930	893.1	904	922.1	930	80–300	C_i [c]
932.1	945	905.9	915	932.1	945		
910.1		881.7		910.1		260–305	C_i-O_i' [d]
942.7		916.3		942.7			
1097.3		1097.3		1048.1			
885		860		885		260–305	C_i-O_i'' [e]
1013.6		982.5		1013.6			
1059.6		1059.6		1007.8			
812.2	811	792	788	812.2	811	270–340	C_i-O_i^* [d]
967.4	934	967.4	933	925.1	892		
1086.2	1087	1051.3	1052	ND	1087		
742.8	759.6	742.3	759.3	709.4	724	270–650	C_iO_i [f]
865.9	861	842.0	836	865.75	861		
1116.3	1114	1079.9	1077	1115.5	1112		

[a]References 2 and 30.
[b]Reference 20.
[c]References 2 and 29.
[d]Reference 26 and this work.
[e]This work.
[f]References 2, 10, and 13.

tal energy of a defective supercell in charge state q, E_V is the valence-band top potential and the term $[E_M(0/+)-E_V]_{expt}$ stands for the experimental donor level (hole emission enthalpy) of the marker (0.28 eV for C_i). Analogously, we may estimate the location of an acceptor level as

$$E_C-E_D(-/0)=A_M(-/0)-A_D(-/0)+[E_C-E_M(-/0)]_{expt},$$

with the help of electron affinities $A_x(-/0)=E_x(-)-E_x(0)$ and the experimentally measured location of the acceptor level $[E_C-E_M(-/0)]_{expt}$ of a marker defect (0.10 eV for C_i).

V. THEORETICAL RESULTS

The ground-state structure of the C_iO_i complex is represented in Fig. 6(a). Both oxygen and carbon atoms are bonded to three Si ligand atoms and share two of them (Si_B and Si_C). The higher electronegativity of carbon compensates for the excess of electrons in oxygen, stabilizing its threefold coordination. This structure was first proposed by Jones and Öberg[17] and it is well accepted among the community. Like in C_i, the carbon atom in C_iO_i produces a fully occupied donor level in the lower half of the gap. A comparison of its ionization energy with that of C_i places $C_iO_i(0/+)$ at E_V +0.41 eV, i.e., only 0.05 eV above the experimental value.[5]

Acceptor activity was also investigated and the calculations confirm that C_iO_i is not an acceptor. That is, it is estimated that $C_iO_i(-/0)$ lies at $E_C+0.15$ eV, and therefore it has a lower electron affinity than the bottom of the conduction band. Our calculations also confirm previous LVM calculations[12,13] by predicting four Si modes below 600 cm^{-1}, one O-related mode at 760 cm^{-1}, and two C-related modes at 861 and 1114 cm^{-1}. Although the carbon-related modes are within a few wave numbers of the experimental observations, local vibrational mode calculations usually have an error bar of a few tens of cm^{-1}. The
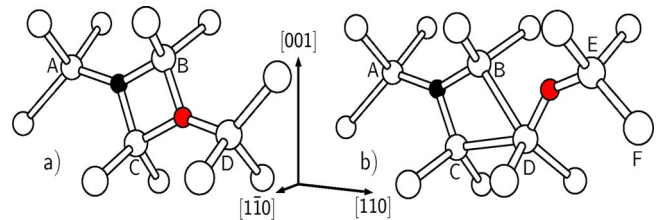

FIG. 6. (Color online) Atomic structures for (a) the ground-state form of C_iO_i and (b) its metastable form $C_iO_i^*$. Silicon, carbon, and oxygen atoms are represented in white, black, and red, respectively. Both complexes possess a common $(1\bar{1}0)$ symmetry plane (C_{1h} point group).

carbon modes are analogous to those arising from the C_i complex, which are observed at 922 and 932 cm^{-1} and calculated at 930 and 945 cm^{-1}, respectively. In Table I we only report the carbon modes of C_iO_i as these are of particular interest in this work.

Now we turn to metastable precursors of C_iO_i. An infinite number of candidates are available so we have restricted our search domain based on the following assumption. We know that twofold- and threefold-coordinated O atoms produce distinct LVM-absorption spectra.[12,13] While the former kind gives rise to modes in the region of 1000 cm^{-1}, the latter vibrates at around 750 cm^{-1}. The measurements indicate that the metastable species produce ^{16}O-related modes at 967, 1060, and 1097 cm^{-1}. Therefore we paid special attention to setting up initial configurations possessing twofold-coordinated Si-O-Si structures. The carbon atom was placed in either trivalent or tetravalent configurations.

The lowest-energy metastable C_i-O_i^* complex is shown in Fig. 6(b) and its total energy is 1 eV above the ground state. In C_i-O_i^* both C and O lie on the same (110) plane and Si$_D$ is overcoordinated. This is judged the best candidate for a precursor of the stable C_iO_i defect. The binding energy C_i-O_i^* (obtained from separate supercell calculations of C_i and O_i) is 0.7 eV. This value is considerably less than the 1.7 eV binding energy for the ground state of C_iO_i, and both figures are in line with their respective thermal stabilities.

Calculated LVM frequencies for the C_i-O_i^* complex considering several C and O isotopes are shown in Table I along with their experimental assignments. The 1086.2 and 812.2 cm^{-1} absorption bands that appear in samples containing mainly ^{12}C isotopes are localized on carbon and are assigned to the 1087 and 811 cm^{-1} modes. The oxygen-related band at 967.4 cm^{-1} is assigned to the 934 cm^{-1} mode. Again, the 1087 and 811 cm^{-1} carbon modes are analogous to the 922 and 932 cm^{-1} modes of C_i. But contrary to C_iO_i, in C_i-O_i^* the twofold-coordinated oxygen-related mode falls between the carbon modes. Table I also reports calculated LVM frequencies for ^{18}O and ^{13}C substitutions, and all agree closely with the measurements.

Calculated ionization energies and electron affinities of C_i-O_i^* and C_i indicate that the former has donor and acceptor levels at 0.11 and 0.02 eV above those of $C_i(0/+)$ and $C_i(-/0)$, placing C_i-$O_i^*(0/+)$ and C_i-$O_i^*(-/0)$ levels at E_V +0.39 eV and E_C−0.08 eV, respectively. These values are in excellent agreement with the DLTS measurements reported in Refs. 26 and 27. The amphoteric character and level positions of this center are not surprising if we think that its electronic structure essentially arises from an oxygen-perturbed C_i center. As in other electrically active oxygen centers (e.g., thermal donors), the electronegative oxygen atom near the electrically active core, C_i in this case, repels its donor and acceptor electrons. Consequently both C_i donor and acceptor levels are slightly shifted upward in the gap.

Other metastable C_i-O_i structures were investigated. *Compact* structures, where O and C atoms share Si ligands, showed LVM frequencies that are not compatible with the sets of absorption frequencies reported in Table I. On the other hand, *remote* structures such as C_i-O_i^* where O and C atoms are separated by at least one Si-Si bond could explain the observations. The short Si$_A$-C and Si$_B$-C bonds in C_i

produce a tensile strain field along [110]. This feature has been shown by measuring the piezospectroscopic strain tensor which is highly tensile along [110].[38] On the other hand, O_i is compressive along [111], and both centers find a local minimum of energy in a *symbiotic* way by strain field exchange when they lie on the same {110} plane. To look at these remote C-O pairs we had to use 216–Si atom supercells. Results from smaller cells suffered from defect-image interaction between neighboring supercells. We placed the O atom between Si$_E$ and Si$_F$ atoms [see Fig. 6(b)]. Upon atomic relaxation we found that this complex is only 0.16 eV less stable than C_i-O_i^*. Local vibrational frequency calculations confirm that in this complex the oxygen mode shifts up to 1038 cm^{-1} and crosses over the highest-frequency carbon mode at 1008 cm^{-1}. This shows fair agreement with the measured absorption frequencies assigned to both C_i-O_i' and C_i-O_i'' (see Table I). It is proposed that the less stable C_iO_i precursors are formed by pairs of C and O atoms lying on the same {110} plane and separated by more than one Si-Si bond.

VI. CONCLUSIONS

Absorption bands produced by several defects incorporating C_i and O_i atoms have been studied in detail. Fourier transform (FT) IR data were obtained from Si samples doped with three combinations of dominant oxygen and carbon isotopes, including the effect of ^{18}O and ^{13}C. Our results on the most stable C_iO_i structure are consistent with those presented in Refs. 12 and 13 and give further support to the model of the C_iO_i defect which consists of a ring structure involving threefold-coordinated oxygen and carbon atoms on the same (110) plane. Experimental results show that in the course of the formation of the stable interstitial carbon–interstitial oxygen defect, three metastable complexes incorporating C_i and O_i atoms occur. Three sets of LVMs were assigned to these complexes on the basis of a similar evolution of the individual set members upon thermal treatments. The incorporation of oxygen and carbon atoms into the complexes is evidenced by the observation of clear shifts of local vibrational modes due to these defects after replacements of ^{16}O and ^{12}C atoms by their isotopes.

Ab initio modeling studies show that in addition to the most stable C_iO_i defect there is a set of metastable structures where C and O atoms are separated by at least two Si atoms. Both C and O atoms lie on a common {110} plane and find a local energy minimum by exchanging strain energy. According to modeling results, the lowest-energy metastable complex, referred to as C_i-O_i^*, has a binding energy of 0.7 eV, accurately reproduces the oxygen- and carbon-related absorption data, and accounts well for the location of the electrical levels that have been measured by DLTS and assigned to a precursor of C_iO_i. More remote C-O pairing results in less stable structures. While the C_iO_i ground state and C_i-O_i^* metastable structures produce an oxygen-related band lying below and between a pair of carbon bands, respectively, the

calculations show that for the less stable C_iO_i precursors the observed O-related band lies above the C-related bands. This feature results from a decrease in the coupling between C and O atoms with increase in their distance, making their properties closer to those when they are found as individual species.

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