Formation and dissociation reactions of complexes involving interstitial carbon and oxygen defects in silicon

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We present a detailed first-principles study which explores the configurational space along the relevant reactions and migration paths involving the formation and dissociation of interstitial carbon-oxygen complexes, $C_i O$ and $C_i O_2$, in silicon. The formation/dissociation mechanisms of $C_i O$ and $C_i O_2$ are found as occurring via capture/emission of mobile $C_i$ impurities by/from O-complexes anchored to the lattice. The lowest activation energies for dissociation of $C_i O$ and $C_i O_2$, into smaller moieties are 2.3 eV and 3.1 eV, respectively. The first is compatible with the observed annealing temperature of $C_i O$, which occurs at around 400 °C, and below the threshold for $O_i$ diffusion. The latter exceeds significantly the measured activation energy for the annealing of $C_i O_2$ ($E_a = 2.55$ eV). We propose that instead of dissociation, the actual annealing mechanism involves the capture of interstitial oxygen by $C_i O_2$, thus being governed by the migration barrier of $O_i$ ($E_m = 2.53$ eV). The study is also accompanied by measurements of hole capture cross sections and capture barriers of $C_i O$ and $C_i O_2$. In combination with previously reported data, we find thermodynamic donor transitions which are directly comparable to the first-principles results. The two levels exhibit close features, conforming to a model where the electronic character of $C_i O_2$ can be described by that of $C_i O$, perturbed by a nearby $O$ atom. [Postprint published in Physical Review Materials 4, 064601 (2020); DOI:10.1103/PhysRevMaterials.4.064601]

I. INTRODUCTION

Understanding the evolution of point defect complexes in silicon (Si) during device processing is highly significant to the industry of electronics and photovoltaics. Carbon and oxygen are the most common foreign species in mono-crystalline Si wafers grown by the Czochralski technique (Cz-Si), with concentrations of about $10^{16}$ cm$^{-3}$ and over $10^{17}$ cm$^{-3}$, respectively. They are predominantly present in the as grown Si material in the form of substitutional carbon ($C_s$) or interstitial oxygen ($O_i$) impurities.

Despite being electrically inert, $C_s$ and $O_i$ can have significant influence on the electrical properties of Si wafers/samples. A conspicuous example is the formation of the so-called thermal double donors, which comprise a family of oxygen aggregates that lead to a considerable increase in the so-called thermal double donors, which comprise a family of oxygen aggregates that lead to a considerable increase in the so-called thermal double donors, which comprise a family of oxygen aggregates that lead to a considerable increase in free-electron concentration. The effect occurs upon heat treatments of O-rich Si in the temperature range of 400-500 °C, while it is strongly suppressed in samples where in addition to oxygen, carbon is also present in a high concentration [1, 2].

Another prominent example is the so-called light-induced-degradation (LID) of n-p-Si solar cells where the p-type layer is boron (B) doped [3, 4]. Recent measurements and theory indicate that the defect comprises a complex made of one boron atom and an oxygen dimer [5].

Both $C_s$ and $O_i$ can trap intrinsic defects, resulting in electrically active complexes that can travel long distances in the Si [6]. Interstitial oxygen comprises a two-fold coordinated O atom sitting near the center of Si-Si bonds. Migration of $O_i$ proceeds via consecutive jumps between nearest bonds with an activation energy $E_m = 2.53$ eV [7]. It is primarily a trap for vacancy-type defects, in particular the mono-vacancy ($V$), thus leading to formation of the vacancy-oxygen complex which has an acceptor level at $E_a = 0.17$ eV [8, 9].

On the other hand, $C_i$ is an efficient trap for self-interstitials ($SI_i$), where $SI_i$ partially takes the place of the C-atom, which is displaced from the substitutional site to become interstitial carbon ($C_i$). This reaction has been termed as kick-out mechanism [10]. $C_i$ shows a split-interstitial configuration, comprising a C-Si dimer sharing a lattice site and aligned along ⟨001⟩ [11–13]. $C_i$ produces both acceptor ($E_a = 0.10$ eV) and donor ($E_d + 0.28$ eV) levels [14] ($E_d$ and $E_v$ denote the conduction and valence band edge energies respectively). The defect becomes mobile just above room-temperature (RT), and depending on doping type, anneals out with an activation energy of $0.7-0.87$ eV (assigned to its migration barrier), yielding a diffusivity in the range $10-15$ cm$^2$/s [11, 15, 16].

In carbon-rich Si, mobile $C_i$ defects are most likely to be captured by $C_s$, forming interstitial-carbon-substitutional-carbon complexes ($C_i C_s$) [17]. In oxygen-rich Si, the dominant trap for the mobile $C_i$ is $O_i$ [18], leading to formation of interstitial-carbon-interstitial-oxygen complexes ($C_i O_i$). $C_i O_i$ has a deep donor level at $E_v + 0.36$ eV, and that has been corroborated by both electron paramagnetic resonance (EPR) and deep-level transient spectroscopy (DLTS) measurements [19, 20]. We should add that substitutional boron ($B_s$) is known to compete with $C_i$ for the capture of $Si_i$ defects by a similar kick-out mechanism, suppressing the generation of $C_i$, and therefore, the formation of $C_i O_i$ [21, 22]. When $B_s$ is the dominant trap, the resulting boron interstitial ($B_i$) defects become mobile at RT and ultimately form $B_i O_i$ and $B_i B_i$ complexes, depending on the relative content of $B_s$ and $O_i$ in the samples [21–24].

$C_i O_i$ has been extensively investigated by several spectroscopic techniques. The defect gives rise to a conspicuous zero-phonon emission line at 789 meV, the so-called C-line in the photoluminescence (PL) spectra, at low temperatures ($T \leq 20$ K) [25–27]. This energy is close to the gap width ($E_g$) subtracted by the hole binding energy of the donor.
level \( (E_{\text{C-line}} \approx E_g - 0.36 \text{ eV}) \), and was interpreted as resulting from the recombination energy of a diffuse electron possessing a conduction-band-like character with a hole tightly bound \((\sim 0.36 \text{ eV binding energy})\) to neutral \( \text{C}_2 \). From Fourier-transform infra-red (FTIR) absorption spectroscopy, two main local vibrational mode (LVM) bands associated with \( \text{C}_2 \) are also well established. At low temperatures, they appear at \( 865 \text{ cm}^{-1} \) (known as \( \text{C}(3) \) band) and at \( 1116 \text{ cm}^{-1} \) \[26, 28–30\]. From \textit{ab-initio} local density functional calculations, Jones and Öberg \[31\] and more recently Coutinho \textit{et al.} \[29\], showed that in the \( \text{C}_2 \) ground state, both \( \text{O} \) and \( \text{C} \) are three-fold coordinated. This configuration was shown to be necessary in order to account for the electrical, optical and magnetic resonance experiments \[19, 26, 28–30\].

More recently, Khirunenko \textit{et al.} \[32, 33\] found that the formation of \( \text{C}_2 \) is more complex than previously thought, and reported the formation of metastable configurations of \( \text{C}_2 \) during isochronal annealing of irradiated Si in the temperature range 280-360 K. These findings were interpreted as the formation of a precursor (labelled \( \text{C}_2 \) ) before reaching the ground state \[32–34\]. The proposed geometry for the metastable defect consisted of \( \text{C}_2 \) and \( \text{O}_2 \) defects lying on a common \{110\} plane and separated by a Si-Si bond, essentially retaining their three-fold and two-fold coordination of their individual structures, respectively. From annealing data, the \( \text{C}_2 \) → \( \text{C}_2 \) conversion was estimated to be activated by a barrier of \( \sim 1 \text{ eV} \) \[34\]. Although capture/transformation/dissociation mechanisms have not been explored by theory, the binding energy of \( \text{C}_2 \) was calculated to be \( \sim 0.7 \text{ eV} \), about 1 eV lower than that estimated for \( \text{C}_2 \) (ground state) \[33\].

The evolution of \( \text{C}_2 \) upon post-irradiation thermal treatments has been studied for decades, but surprisingly, few studies addressed the kinetics and annealing mechanisms of \( \text{C}_2 \). The defect is generally considered to be stable up to 400 °C \[22, 27, 28\]. By monitoring the \( \text{C}(3) \) absorption band in high-fluence MeV electron-irradiated Cz samples \[28\], first order annealing kinetics was inferred with activation energy and pre-factor (of the order of the Debye frequency of Si), it was suggested that the annealing of \( \text{C}_2 \) occurs via dissociation, rather than being a diffusion-limited process. To clarify this and other issues related to the formation and dissociation of carbon-oxygen complexes, we performed a detailed theoretical study which explores the configurational space along relevant reaction and migration paths involving \( \text{C} \) and \( \text{O} \) species in Si. The study is also accompanied by measurements of capture cross-sections and barriers for the capture of holes by \( \text{C}_2 \) and \( \text{C}_2 \), allowing us to accurately locate their thermodynamic donor transition.

**II. METHOD DETAILS**

**A. Calculation details**

First-principles calculations were performed using the Vienna \textit{ab-initio} Simulation Package (VASP) \[42–45\], employing the projector-augmented wave (PAW) method for the treatment of the core electrons \[46\]. A basis set of plane-waves with kinetic energy of up to 400 eV was used to describe the Kohn-Sham states. All many-body energies reported were evaluated self-consistently, using the hybrid density functional of Heyd-Scuseria-Ernzerhof (HSE06) \[47, 48\], up to a numerical accuracy of \( 10^{-7} \) eV. Hybrid density functionals perform relatively better in terms of the calculated band structure, when compared with semi-local functionals, including those using the generalized gradient approximation (GGA) \[49\]. The GGA was however employed for the search of ground-state and saddle-point structures along the minimum energy paths (MEP) of atomistic mechanisms. All structures were optimized until forces on atoms were below 0.01 eV/Å. The two-step method — firstly involving a calculation of a GGA-level structure followed by a single-point energy calculation within HSE06, was shown to lead to numerical error bars below 10 meV for relative energies, including formation energies and migration barriers \[50, 51\]. These tests also apply to the methods used below to find saddle point energies, which are simply a sequence of structural relaxations subject to a particular set of constraints.
We used 216-atom supercells of silicon (with cubic shape), obtained by replication of $3 \times 3 \times 3$ conventional cells, in which carbon and oxygen atoms were inserted to produce CO-related defects. The defects considered were all interstitials, namely carbon (C), oxygen (O), carbon-oxygen dimers ($O_2$), carbon-oxygen ($C_2O$), and carbon-dioxide ($CO_2$). The equilibrium (calculated) lattice parameters of Si was $a = 5.4318$ Å, matching the experimental value of $a = 5.4310$ Å. The Brillouin zone (BZ) of GGA- and HSE06-level calculations was sampled at $\Gamma$centered $2 \times 2 \times 2$ ($\Gamma$-2$^3$) and $1 \times 1 \times 1$ ($\Gamma$-point) k-point meshes, respectively.

To investigate defect migration and transformation processes, we employed a combination of nudged elastic band (NEB) [52, 53] and dimer [54] methods (at the GGA level). For the NEB calculations, initial and final (frozen) geometries were at the limits of a sequence of 9-11 intermediate images, which were created at first hand by linear interpolation and adjusted to avoid unphysical bond lengths. Saddle-point search calculations involved a first step consisting of a fast exploratory NEB run with the Brillouin zone being sampled at the $\Gamma$-point. On a subsequent step, we increased the k-point sampling density to $\Gamma$-2$^3$, and refined the exploratory MEP by either employing the climbing-image NEB method [55] or by performing a dimer search. The dimer run was initiated using the two higher-energy structures obtained from the previous exploratory NEB step. Finally, the resulting highest-energy configuration along each MEP (the saddle point) was taken in order to calculate its total energy within HSE06.

**B. Measurement details**

A set of $n^+ p$ diodes were prepared (fabrication details are described in Ref. [41]) on a p-type (boron doped) Cz-Si wafer with resistivity of $\sim 14$ Ω cm, corresponding to a net carrier concentration of about $\sim 1 \times 10^{15}$ cm$^{-3}$ at RT, as determined by capacitance-voltage (C-V) measurements with a 1MHz probe frequency. The oxygen and carbon concentration in the wafers was $7 \times 10^{17}$ cm$^{-3}$ and $\leq 2 \times 10^{16}$ cm$^{-3}$, respectively, as determined by secondary ion mass spectrometry (SIMS). Aluminum (Al) Ohmic contacts were deposited by electron beam evaporation on the front side ($n^+$ layer) and silver paste was applied on the back side of the samples to form an Ohmic contact. The fabricated $n^+ p$ diodes were subjected to annealing at 300 °C for 26 h in N$_2$ atmosphere and then were irradiated with 1.8 MeV protons at RT to doses of $1 \times 10^{13}$ cm$^{-2}$. After irradiation, the samples were annealed at 400 °C for 1.5 h in order to anneal out all the radiation-produced point defects, except C$_2O$, which exhibited a dominating DLTS peak. One of the samples was subjected to a multiple-step annealing at 400 °C for about 30 h in total in order to achieve a complete annealing of the C$_2O$ complex and formation of C$_2O_2$ (see Ref. [41] for further details). C-V and DLTS measurements were employed after each annealing step for characterizing the samples using a refined version of the setup described in Ref. [56], equipped with a closed-cycle He cryostat.

In DLTS, the reverse bias quiescent voltage was kept at $-10$ V, the filling pulse was 50 ms long at 0 V bias, and the sample temperature was scanned between 50 K and 300 K. The DLTS signal was extracted from the recorded capacitance transients applying a lock-in and a high resolution weighting function, so-called GS4 [57], with six different rate windows in the range of $(20-640\text{ms})^{-1}$. The C$_2O$ and C$_2O_2$ defects were monitored via their respective deep levels at $E_v + 0.36$ eV and $E_v + 0.39$ eV. These correspond to DLTS peak positions at 173 K and 190 K, respectively, when employing a rate window of 640 ms$^{-1}$ and the GS4 weighting functions. Hole capture cross sections ($\sigma$) were measured for C$_2O$ and C$_2O_2$ traps by varying the filling pulse duration from 10 ns to 10 $\mu$s and recording the amplitude of the level signal. During these measurements a single rate window was used for each capture cross section measurement and the sample temperature was kept constant within $T = T_{\text{max}} \pm 0.1$ K, where $T_{\text{max}}$ is the temperature that corresponds to to maximum DLTS signal for a specific rate window.

**III. RESULTS**

**A. Migration energies of elementary defects**

We start by reporting on some properties of basic elements that participate in the reactions addressed in Sec. III B, namely O, O$_2$, C, C$_2$, O$_3$ and C$_2$O$_2$.

In agreement with previous experimental and theoretical studies [11–13, 58], we find that the ground-state structure of interstitial carbon (C$_i$) in Si comprises a C-Si split-interstitial, possessing dangling bonds on both C and Si atoms. As shown in Figs. 1(a) and 1(b), the C-Si dimer is aligned along the ⟨001⟩ direction, and both atoms share a lattice site.
As for interstitial oxygen (O$_i$) in Si, the resulting ground state structure is also in line with the widely accepted model, according to which the O atom sits near the bond center site, forming a *puckered* Si-O-Si unit [59–61]. The orbiting motion of the O atom around the (111) axis of the perfect Si-Si bond, as well as its motion across the bond center site, involve surmounting rather shallow energy barriers of the order of 10 meV.

The minimum-energy structure of the oxygen dimer is the so-called *staggered* configuration [60–62], where two O atoms occupy neighboring bond center sites, thus connecting to a common Si atom. In this geometry, the O atoms in the Si-O-Si-O-Si structure are displaced in a staggered way. This minimizes the departure from the sp$^3$ bond angles involving the central Si atom and its O neighbors [60–62].

For the C$_i$O$_2$ and C$_i$O$_{2i}$ complexes, we found that in both cases the defect core comprises a square-like structure involving C, O and two Si atoms. Figs. 1(c) and 1(d) represent two orientations of C$_i$O$_2$ in Si. For the case of C$_i$O$_{2i}$, the structure is similar to that of C$_i$O$_2$, although an additional O atom is connected to Si atoms number 4 and 5 in Figs. 1(c). Hence, the complex is essentially a staggered O$_2i$ next to C$_i$.

We also found a metastable C$_i$O$^\ast$ complex, identical to that reported by Khirunenko et al. [33], consisting of C$_i$ and two-fold coordinated O$_i$ impurities separated by a Si-Si bond and sharing the same plane. The C$_i$O$^\ast$ complex was found 1.0 eV above the ground state, *i.e.*, with a binding energy of 0.56 eV with respect to isolated C$_i$ and O$_i$ impurities.

In the analysis of the defect reactions described in Sec. III B, we assume that the migration barriers for C$_i$, O$_i$ and O$_{2i}$ are respectively (0.73 ± 0.05) eV, (2.53 ± 0.03) eV and (2.02 ± 0.01) eV as derived from experiments [63–65]. The migration mechanisms of all three defects are well established theoretically [61, 66]. Hence, a calculation of the respective barriers would provide us with an idea of the error bar of the methodology. As mentioned in Sec. II A, the search for saddle-points was conducted along the configurational space between initial and final ground states structures.

The MEP for migration of C$_i$ was found to involve a change in the defect alignment within the Si lattice. Initial and final configurations are illustrated in Figs. 1(a) and 1(b). Accordingly, the C atom performs an *out-of-plane* jump, leading to a change of orientation of the main (100) symmetry axis. This mechanism was earlier found by Capaz et al. [66], and according to our calculations corresponds to a MEP with a total barrier of $E_m = 0.76$ eV. This figure matches recent annealing experiments carried out in n$^+$-p-diodes under reverse bias [63], where a barrier for the migration of carbon interstitial in the neutral charge state was measured as $E_m = 0.73$ eV. The energy barrier for the *in-plane* jump of C$_i$ is about 1.6 eV high, essentially due to the fact that the carbon atom has to travel through a high-energy two-fold coordinated Si-C-Si structure.

Interstitial oxygen migrates by hopping between neighboring (puckered) bond center sites. The saddle-point configuration is commonly referred to as Y-lid [61], and it is analogous to the stable configuration of C$_i$ depicted in Figure 1 (the C atom being replaced by O). Our calculations indicate that the Y-lid structure of O$_i$ is 2.63 eV above the ground state, overestimating the experimental figure by a mere 0.1 eV. This result is in line with the 2.7 eV barrier height reported previously using hybrid density functional calculations [67]. As for the oxygen dimer, the saddle-point for migration is attained when both O atoms display three-fold coordination (see Figure 7 on Ref [61]). Here we found that the relevant structure along the path is 1.87 eV above the ground state, about 0.1 eV below the measured value [65]. These results suggest that the error bar regarding the energy barriers to be discussed below is about 0.1 eV. This is approximately twice the error in the measured barrier of O$_i$ and about 10 times the error in the measured barriers of O$_i$ and O$_{2i}$ [63–65].

Like the carbon interstitial, the MEP for migration C$_i$O$_i$ also involves a change in the defect alignment within the Si lattice. Initial and final configurations are shown in Figs. 1(c) and 1(d). C and O atoms in C$_i$O$_i$ jump off the {110} symmetry plane, in a sequential manner — first the carbon atom, then the oxygen. The second step has the highest barrier, leading to an overall migration barrier of $E_m = 2.45$ eV. This is 0.65 eV lower than the barrier for in-plane migration, and such a large figure derives from the nearly independent jump of the O atom.

Below we will argue that migration of C$_i$O$_i$ is actually an unlikely event due to the fact that dissociation is governed by a lower barrier. An analogous argument applies to C$_i$O$_{2i}$.

**B. Formation and dissociation of C$_i$O$_i$ and C$_i$O$_{2i}$**

Before proceeding, we leave a few words about notation. Let us consider that A and B stand for either O$_i$, C$_i$ or a complex made of any (including more than one) of these species. Infinitely separated defects A and B are represented as A+B (*e.g.* C$_i$O$_i$+O$_i$); Complexes involving close pairs of A and B atoms separated by two or more Si atoms, but still sharing the same supercell volume, are represented as A-B (*e.g.* C$_i$O$_i$-O$_i$); Complexes involving A and B moieties connected to a common Si atom are termed AB (*e.g.* C$_i$O$_{2i}$). We did not find stable complexes involving direct C-O or O-O bonds. Di-carbon complexes were not investigated.

Regarding the designation of the saddle-point structure along a particular MEP, we found it useful to highlight the atoms that move most during the respective mechanism. This is done by enclosing the moving species within parentheses. For the dissociation of C$_i$O$_{2i}$, for instance, if the jumping moiety is the carbon atom (leaving O$_{2i}$ behind), the carbon species is enclosed within parentheses. Hence, a first-step for the dissociation reaction is cast as

$$C_iO_{2i}(C_i)^O_{2i} \rightarrow C_i-O_{2i},$$

which involves a detachment of the carbon atom from O$_{2i}$, followed by a second step

$$C_i-O_{2i}(C_i)^O_2 \rightarrow C_i + O_{2i},$$

describing the migration of C$_i$ away from O$_{2i}$. 

Figure 2. Reaction energy diagram involving interstitial carbon (C<sub>i</sub>) and two interstitial oxygen impurities (O<sub>i</sub>) in silicon. The diagram highlights in red and blue the most favorable reactions paths describing the formation/dissociation of C<sub>i</sub>O<sub>i</sub> and C<sub>i</sub>O<sub>2i</sub> complexes, respectively. Reactions proceed through sequential transformations between reaction steps denoted with letters ‘A-E’. These correspond to stable states represented by a thick horizontal segment, a state label and its relative energy within square brackets. See text for details regarding label notation. Intermediate states (between stable steps) are saddle-points and correspond to the summit of the minimum energy path that separates neighboring stable states. Atoms or groups of atoms that jump during each step are represented within parentheses. The origin of the energy coordinate is shown as a dashed horizontal line. All energies are in eV.

Figure 2 shows a reaction energy diagram accounting for the interactions between one C and two O atoms in silicon. Each state involves three interstitial atoms, being represented by a horizontal segment in the energy scale, a state label and its relative energy, in eV, enclosed within square brackets. Starred energies were obtained with help of experimentally obtained migration barriers of C<sub>i</sub>, O<sub>i</sub> and O<sub>2i</sub>. All energies are relative to the C<sub>i</sub>+O<sub>i</sub>+O<sub>i</sub> state in step A. This is indicated by the wide horizontal dashed line, and stands for uncorrelated C<sub>i</sub> and two O<sub>i</sub> impurities. Each step (A-E) groups one or more stable (ground or metastable) states. Different states within each step are not necessarily close in configurational space. States between neighboring steps are saddle-points. The purpose of the thin lines connecting the horizontal state segments is to relate every pair of stable states with at least one saddle point. They also provide guidance to the reader in the identification of mechanisms along the reactions steps. The atoms that move most during a transition are enclosed within parentheses (see above).

Figure 2 also highlights the most favorable reactions paths for the formation/dissociation of C<sub>i</sub>O<sub>i</sub> (A ↔ C) and C<sub>i</sub>O<sub>2i</sub> (C ↔ E) complexes in red and blue, respectively. Formation and dissociation processes read from left to right and vice versa, respectively. The ground states in steps C and E correspond to the C<sub>i</sub>O<sub>i</sub> and C<sub>i</sub>O<sub>2i</sub> complexes, respectively. From their relative energies we find that the binding energies of C<sub>i</sub> to O<sub>i</sub> and to O<sub>2i</sub> are E<sub>b</sub> = 1.56 eV and 2.33 eV as obtained from the energy balance of:

\[
C_i + O_i + O_i (A) \rightarrow C_iO_i + O_i (C) + [E_b = 1.56\text{eV}] \quad (3)
\]

and

\[
C_i + O_{2i} (C) \rightarrow C_iO_{2i} (E) + [E_b = 2.33\text{eV}], \quad (4)
\]

respectively, where reaction steps are indicated within parentheses. The magnitude of the binding energies indicate a strong thermodynamic drive for formation of these complexes. The binding energy of C<sub>i</sub>O<sub>i</sub> is also in line with previous calculations, where E<sub>b</sub> values were found in the range 1.6-1.7 eV [29, 33, 68]. The binding energy between two interstitial O atoms is found from the energy difference of states in steps A and C, namely

\[
C_i + O_i + O_i (A) \rightarrow C_i + O_{2i} (C) + E_b, \quad (5)
\]

with E<sub>b</sub> = 0.33 eV, nicely matching the 0.3 eV found experimentally by Murin et al. [69].

Migration barriers of C<sub>i</sub> (0.73 eV), O<sub>i</sub> (2.53 eV), O<sub>2i</sub> (2.02 eV) and C<sub>i</sub>O<sub>i</sub> (2.45 eV) were considered for the saddle-point transitions A → B and C → D. The reactants are at least two independent defects, one of which is a diffusing species (indicated within parentheses). The products involve metastable precursors (steps B and D) that can be converted into stable defects in steps C and E, respectively. The mechanisms and saddle-points for these conversions, namely B → C...
and D \rightarrow E$, are indicated between the respective reaction steps. Again, the moving atoms are enclosed within parentheses.

The minimum energy path for formation of C$_{\text{O}}$ is clearly limited by the migration barrier of C$_{\text{i}}$ and not by a capture barrier. This is compatible with the observation of C$_{\text{O}}$ in irradiated material at room-temperature. Accordingly, the saddle point energy for the migration of C$_{\text{i}}$ is located at 0.18 eV in the energy scale, below the 0.76 eV of the state involving the migration of C$_{\text{i}}$. Obviously, the large migration barrier of O$_{\text{i}}$ inhibits the formation of C$_{\text{O}}$ via migration of oxygen.

Note that the left reactant in Reaction 6 is distinct from the metastable C$_{\text{O}}^*$ precursor reported in Ref. [33]. In the C$_{\text{O}}$ structure, both C and O atoms are separated by a Si-Si bond, but unlike C$_{\text{O}}^*$, they do not share the same crystallographic plane. According to the energy scale of Figure 2, C$_{\text{O}}^*$ is located at $-0.56$ eV. Direct conversion of C$_{\text{O}}^*$ into C$_{\text{O}}$ via in-plane jump of carbon or oxygen atoms involves surmounting a barrier of at least 2.0 eV. Alternatively, the transformation of C$_{\text{O}}^*$ firstly into triclinic C$_{\text{O}}$ (step B) followed by conversion into C$_{\text{O}}$ (step C) has an overall barrier of only 0.94 eV. This is in excellent agreement with the measurements of Abdullin et al. [34], who reported a 1 eV activation energy for the growth of C$_{\text{O}}$ DLTS signal at the expense of another peak related to its precursor.

Dissociation of C$_{\text{O}}$ essentially consists of the reversed formation mechanism (red line in Figure 2). The overall activation energy for dissociation, $E_d = 2.29$ eV, is also governed by the migration of C$_{\text{i}}$, which follows from its off-plane detachment from oxygen in a first stage (reversal of the reaction 6). This result slightly overestimates the $\sim 2$ eV from early measurements of the activation energy for the annealing of C$_{\text{O}}$ [28, 70].

The alternative mechanism, where instead of C$_{\text{i}}$ motion, the first stage involves a detachment of O$_{\text{i}}$ from C$_{\text{O}}$,

$$C_{\text{O}} + O_{\text{i}} (C) \overset{C_{\text{i}}O_{\text{O}} + O_{\text{i}}}{\rightarrow} C_{\text{O}} + O_{\text{i}} (B), \tag{7}$$

was also inspected. Reaction 7 starts from ground state at step C (red) and has a barrier of 2.07 eV with saddle-point at $+0.51$ eV shown in Figure 2 in black. However, since C$_{\text{i}}$ still has to escape from oxygen, the overall barrier for dissociation is also $E_d = 2.29$ eV. This dissociation route is nevertheless unlikely to occur due to a higher first stage barrier.

Now we turn to C$_{\text{O}_2}$. Its formation can occur either (i) via further accumulation of oxygen in C$_{\text{O}_i}$, which means starting with reactants C$_{\text{O}_i} + O_{\text{i}}$ (step C, red line) in Figure 2, or (ii) from reaction between C$_{\text{i}}$ and O$_{\text{2i}}$, where the starting conditions are represented by C$_{\text{i}} + O_{\text{2i}}$ (step C, blue line). Of course, in C$_2$Si, where the concentration of oxygen is much larger than that of carbon, the initial state of option (ii) can only be achieved upon release of C$_{\text{i}}$ defects from the overwhelming concentration of oxygen traps. Hence, option (ii) actually involves two simultaneous reactions, namely (ii.1) the dissociation of C$_{\text{O}_i}$ (reaction C $\rightarrow$ A) and (ii.2) capture of C$_{\text{i}}$ by O$_{\text{2i}}$ to the more stable C$_{\text{O}_2}$ complex (reaction C $\rightarrow$ E).

The alternative formation mechanism implying the capture of a diffusing O$_{\text{2i}}$ by C$_{\text{i}}$ is not physically probable due to the high barrier involved.

According to Figure 2, the formation mechanism (i) can occur via migration of O$_{\text{i}}$ with an overall barrier of 2.53 eV, or via migration of C$_{\text{O}_i}$ with an activation energy of 2.45 eV. However, these reaction routes are shortcut by dissociation of C$_{\text{O}_i}$ (which has an energy barrier of 2.29 eV only), thus providing the necessary conditions for activation of the formation mechanism (ii). Like C$_{\text{O}_i}$, the formation of C$_{\text{O}_2}$ via mechanism (ii) along the blue line of Figure 2 is only limited by the migration barrier of C$_{\text{i}}$. However, because the first stage reaction (ii.1) actually involves the dissociation of C$_{\text{O}_i}$ (reaction C $\rightarrow$ A), the formation mechanism of C$_{\text{O}_2}$ is effectively activated by the dissociation barrier of C$_{\text{O}_i}$, i.e., $E_a = 2.29$ eV. Note that the state (C$_{\text{i}}$) + O$_{\text{i}}$ + O$_{\text{2i}}$ at 0.73 eV which limits the dissociation of C$_{\text{O}_i}$ to make carbon interstitials available, is higher in energy than (C$_{\text{i}}$) + O$_{\text{2i}}$ at 0.40 eV governing the capture of C$_{\text{i}}$ by O$_{\text{2i}}$. This picture explains the observed correlation between the dissociation of C$_{\text{O}_i}$ and formation of C$_{\text{O}_2}$ [39–41].

Regarding the dissociation of C$_{\text{O}_2}$, we calculated four possible scenarios which differ in the initial E $\rightarrow$ D step as depicted in Figure 2, and can be summarized as follows: (i) jump of C$_{\text{i}}$ away from C$_{\text{O}_2}$, leaving O$_{\text{2i}}$ behind; (2) detachment of O$_{\text{i}}$ from C$_{\text{O}_2}$ leaving a C$_{\text{O}}$ complex; (3) jump of O$_{\text{i}}$ away from C$_{\text{O}_2}$, leaving a C$_{\text{i}}$ defect, and (4) detachment of a C$_{\text{O}_2}$ complex from C$_{\text{O}_2}$, thus leaving O$_{\text{i}}$. Figure 2 clearly indicates that mechanism (i) is the most favorable dissociation route, showing an activation energy of $E_a = 3.06$ eV. This figure is about 0.5 eV higher than what was recently observed by some of us during annealing experiments [41]. We can only reconcile the calculations with the measurements if we assume that, instead of a dissociation, the relevant annealing mechanism involves the capture of interstitial oxygen by C$_{\text{O}_2}$, namely

$$C_{\text{O}_2} + O_{\text{i}} \overset{C_{\text{O}_2} + O_{\text{i}}}{\rightarrow} C_{\text{O}_3}. \tag{8}$$

thus explaining the measured activation energy $E_a = 2.55$ eV for the annealing of C$_{\text{O}_2}$ [41], which is virtually identical to the migration barrier of O$_{\text{i}}$. We found that the formation of C$_{\text{O}_3}$ according to Reaction 8 is energetically favorable and corresponds to a lowering of the energy by $E_b = 0.76$ eV. Here the ground state structure of C$_{\text{O}_3}$ consisted of a staggered oxygen trimmer next to C$_{\text{i}}$. The binding energy of C$_{\text{i}}$ to O$_{\text{3i}}$ was calculated as $E_b = 2.56$ eV. This figure follows the trend shown by $E_b = 2.33$ eV and 1.56 eV as obtained for the analogous quantity regarding the attachment of C$_{\text{i}}$ to O$_{2i}$ and O$_{\text{i}}$, respectively (see Reactions 3 and 4). The proposed mechanism as described by Reaction 8 is also compliant with the observed first order kinetics of the annealing — the huge concentration of O$_{\text{i}}$ is effectively invariant during the process.

In Ref. [41], an attempt rate for the annealing kinetics of C$_{\text{O}_2}$ was measured as $v_\infty = (2-30) \times 10^{12}$ s$^{-1}$. This figure is
in line with the Debye frequency of Si, suggesting that the annealing should be prompted by atomic vibrations. However, our proposal, according to which C\textsubscript{1}O\textsubscript{2} anneals out due to capture of mobile O\textsubscript{i} impurities is challenged by the fact that \nu\textsubscript{e} is two orders of magnitude slower than the analogous figure obtained for O\textsubscript{i} diffusivity in silicon [7]. The latter is obviously too high to be described as a simple phonon-assisted jump and, as far as we know, there is no clear explanation for such anomaly. At the moment we can only infer that the forward rate of Reaction 8 is limited by a phonon-assisted process, and therefore governed by a physics that somehow differs from that of the migration of isolated O\textsubscript{i}. Hence, while the activation energy for the annealing of C\textsubscript{1}O\textsubscript{2} corresponds to the large migration barrier of oxygen at remote locations from C\textsubscript{1}O\textsubscript{2}, the measured attempt frequency in the 10\textsuperscript{13}-Hz range may simply reflect the kinetics of the slower final steps, when both impurities are in close proximity, which cannot be described as isolated O\textsubscript{i} jumps anymore, but rather as a restructuring of a C\textsubscript{1}O\textsubscript{3i} complex.

We end this section with a few considerations on the charge state dependence of formation and dissociation of C\textsubscript{1}O\textsubscript{i} and C\textsubscript{1}O\textsubscript{2i} complexes. Firstly, the above results refer to neutral defects and essentially they are valid for intrinsic material or doped-Si subject to annealing (\textit{T} \sim 300-500\degree C).

Secondly, we note that the formation and dissociation mechanisms do not involve long range Coulomb interactions between reactants. Hence, in p-type or n-type Si, the energies of the stable states in steps A, C and E should be lowered by an amount that corresponds to the depth of the hole or electron traps of C\textsubscript{1}, C\textsubscript{1}O\textsubscript{i}, or C\textsubscript{1}O\textsubscript{2i}. Analogously, saddle-point energies should consider a charge state effect. In this case, both ‘red’ and ‘blue’ MEPs of Figure 2 are limited by the migration barrier of C\textsubscript{i}. Therefore, if the thermodynamic conditions are such that the Fermi level is above \E\textsubscript{c} \sim 0.12 eV [58] or below \E\textsubscript{c} + 0.28 eV [12], the C\textsubscript{i} defect is negatively or positively charged, so that migration barriers for C\textsuperscript{−}\textsubscript{i} or C\textsuperscript{+}\textsubscript{i} should be considered, respectively. For instance, in heavily-doped p-type Si, the migration barrier of C\textsuperscript{+}\textsubscript{i} was measured as \E\textsubscript{m} = 0.89 eV. Considering the hole trap energies of C\textsubscript{i} (\E\textsubscript{v} + 0.28 eV) and C\textsubscript{1}O\textsubscript{i} (\E\textsubscript{v} + 0.36 eV), we estimate activation energies for formation and dissociation of C\textsubscript{1}O\textsubscript{i} of \E\textsubscript{a} = 0.89 eV and \E\textsubscript{b} = 2.53 eV, respectively. These figures are slightly larger than the analogous quantities reported above for neutral defects (0.73 eV and 2.29 eV, respectively).

### C. Electronic properties

In a recent study, \{C\textsubscript{1},O\textsubscript{i}\}-rich Si samples were irradiation at room-temperature and annealed at 400 \degree C for 30 h in order to anneal out C\textsubscript{1}O\textsubscript{i} and form the C\textsubscript{1}O\textsubscript{2i} [41]. The evolution of the defects was monitored by DLTS via observation of the corresponding hole traps with activation energy for hole emission of \Delta\E\textsubscript{a} = 0.36 eV and \Delta\E\textsubscript{b} = 0.39 eV. In order to obtain the thermodynamic transition levels, a capture barrier has to be subtracted from \Delta\E\textsubscript{b} values, and after that we can compute the observed transitions with corresponding calculations based on ground state energies. Below we present results from measurements of the capture barriers of C\textsubscript{1}O\textsubscript{i} and C\textsubscript{1}O\textsubscript{2i}, which supplement the study of Ref. [41].

The hole capture cross section (\sigma) of C\textsubscript{1}O\textsubscript{i} and C\textsubscript{1}O\textsubscript{2i} was measured at different temperatures and compared for both complexes. Values of \sigma as a function of the inverse of the absolute temperature are plotted in Fig. 3. The \sigma values were extracted from the observed amplitude of the DLTS peak as a function of the filling pulse duration (between 10 ns and 10 \mu s) at sample temperatures in the range 170-215 K. For very short pulses (10-300 ns), the number of filled C\textsubscript{1}O\textsubscript{i} and C\textsubscript{1}O\textsubscript{2i} traps was negligible. On the other hand, for pulses longer than \mu s both signals saturated due to complete filling of the traps. The two levels exhibit close capture cross sections (<9 \times 10\textsuperscript{-17} cm\textsuperscript{2} for C\textsubscript{1}O\textsubscript{i} versus <8 \times 10\textsuperscript{-17} cm\textsuperscript{2} for C\textsubscript{1}O\textsubscript{2i}) with very weak impact of the temperature variation. However, \sigma is a temperature-dependent quantity which can be described as

\begin{equation}
\sigma = \sigma_{\infty} \exp(-\Delta\E_{\sigma}/k_{B}T),
\end{equation}

where \sigma_{\infty} is the direct capture cross section (high temperature limit), \Delta\E_{\sigma} is the thermally activated hole capture barrier and \kB the Boltzmann constant. Values of \Delta\E_{\sigma} and \sigma_{\infty} for C\textsubscript{1}O\textsubscript{i} and C\textsubscript{1}O\textsubscript{2i} were extracted by fitting Eq. 9 to the measured data as depicted in Fig. 3. We found that \Delta\E_{\sigma} is very small and almost identical for both defects, <3 meV for C\textsubscript{1}O\textsubscript{i} and <4 meV for C\textsubscript{1}O\textsubscript{2i}. This result is in line with the model where the C\textsubscript{1}O\textsubscript{2i} hole trap can be described as a C\textsubscript{1}O\textsubscript{i} trap perturbed by the presence of a nearby interstitial oxygen atom.

Activation energies of hole emission and apparent capture cross sections for C\textsubscript{1}O\textsubscript{i} and C\textsubscript{1}O\textsubscript{2i} as reported in Ref. [41] are listed in Table 1. These data are also accompanied by direct capture cross sections and capture barriers for both complexes as obtained from the present measurements. In addition, the measured and calculated (see below) electronic levels
Table I. Activation energies for hole emission ($\Delta E_h$) and apparent capture cross sections ($\sigma$) (from Ref. [41]), direct capture cross sections ($\sigma'$) and capture barriers ($\Delta E_d$) (this work) of C$_i$O and C$_i$O$_{2i}$ complexes in Si. Capture cross sections and energies are given in cm$^2$ and eV, respectively. Measured and calculated donor levels, $E(0^+/+) - E_v$, are also reported.

|        | $\Delta E_h$ | $\sigma$ | $\sigma'$ | $\Delta E_d$ | Measured | Calculated |
|--------|--------------|----------|-----------|--------------|----------|------------|
| C$_i$O | 0.36         | $1 \times 10^{-15}$ | $1.1 \times 10^{-16}$ | 0.003       | 0.36     | 0.30       |
| C$_i$O$_{2i}$ | 0.39   | $2 \times 10^{-15}$ | $9.6 \times 10^{-17}$ | 0.004       | 0.39     | 0.33       |

$[E(0^+/+) - E_v]$ of C$_i$O and C$_i$O$_{2i}$ are also included.

The capture barriers for C$_i$O, and C$_i$O$_{2i}$ are very small, and therefore, the measured activation energies for hole emission essentially represent the location of the donor transition with respect to the valence band top. Furthermore, no variation was found for the hole emission rate of both C$_i$O, and C$_i$O$_{2i}$ traps with the application of different electric fields during the DLTS experiments. The lack of a Poole-Frenkel effect indicates that both levels are likely to correspond to donor transitions.

A transition level between two charge states, say $q$ and $q'$, of a defect (with $q$ more negative than $q'$) is defined as

$$E(q/q') = -\frac{E(q)(R) - E(q')(R')}{q - q'}, \quad (10)$$

where $E(q)$ is the energy of the supercell with the defect in charge state $q$ and $R$ a generalized coordinate representative of the defect configuration. Equation (10) accounts for the fact that charge states $q$ and $q'$ may correspond to radically different atomistic geometries $R$ and $R'$, respectively (which is not the present case). The use of periodic boundary conditions imply that the supercell is always neutral irrespectively of the number of electrons in the system. To mitigate this spurious effect, energies in Eq. (10) are off-set by a periodic charge correction according to Freysoldt et al. [71].

In order to cast the levels in a way that they can be compared to the experiments, i.e., $E(0^+/+) - E_v$, we have to calculate the energy of the valence band top. This is done by using Eq. (10) for the case of a bulk (defect-free) supercell, $E_v = E_{\text{bulk}}(0^+/+)$. The calculated donor levels of C$_i$O, and C$_i$O$_{2i}$ are shown in the right-most column of Table I. They are underestimated with respect to the observations by 60 meV, but significantly, they account for the observed relative depth, i.e., the donor transition of C$_i$O$_{2i}$ is 30 meV above the donor transition of C$_i$O.

The hole traps arise from a fully occupied p-like state centered on the carbon atom, and lying deep in the band gap. Figure 4 depicts the donor state (Kohn-Sham state) within the gap in the form of an electron density isosurface (blue), related to the highest occupied state of neutral C$_i$O, and C$_i$O$_{2i}$ defects. The carbon atom is hidden by the large p-orbital-like shape near the arrow that indicates the [110] direction. There is no apparent difference between the two defects. This is consistent with the nearly identical characteristics determined for both, namely the activation energy for hole emission, the capture barriers and capture cross sections.

The fact that the donor level of C$_i$O$_{2i}$ is slightly higher (30 meV) in the gap, can be explained by the repulsion of the donor electrons on the p-state by the additional and highly electronegative O atom. This effect is analogous to that invoked to explain the raise of the donor transitions of the thermal double donors in Si and Ge, where the increasing number of oxygen atoms accumulated on each donor leads to progressively shallower levels [72].

**IV. CONCLUSIONS**

We presented a detailed model regarding the formation and dissociation mechanisms of carbon-oxygen complexes, involving interstitial carbon and interstitial oxygen impurities. The results are based on hybrid density functional theory. We also supplement previous experimental data with capture kinetics measurements, which allowed us to estimate and compare the capture barriers of C$_i$O, and C$_i$O$_{2i}$.

Like C$_i$O, the C$_i$O$_{2i}$ complex is made of a square-like structure involving C, O and two Si atoms. Both defects show large binding energies,

$$C_1 + O_1 + O_1 \xrightarrow{E_m=0.73\text{eV}} C_1O_1 + O_1 + [E_b = 1.56\text{eV}],$$

$$C_1 + O_{2i} \xrightarrow{E_m=0.73\text{eV}} C_1O_{2i} + [E_b = 2.33\text{eV}],$$
which are suggestive of a high thermal stability. The kinetics of both reactions above are thermally activated by the migration barrier of $C_i$ ($E_{m} = 0.73$ eV). However, in O-rich material and below the annealing temperature of $C_iO_2$ ($\sim 400$ °C), Reaction 11 will dominate due to the large concentration of $O$ traps for the fast-diffusing $C_i$ (in comparison to the concentration of $O_{2i}$).

Dissociation of $C_iO_2$ is simply governed by Reaction 11 in the backwards direction. Now the carbon detaches and escapes from $O_i$. The calculated overall barrier is $E_d = 1.56 + 0.73 = 2.29$ eV. This result implies that $C_iO_2$ should dissociate at a slightly lower temperature than that for migration of $O_i$ (with an activation barrier of about 2.5 eV).

As referred above, around room temperature, $C_i$ defects become mobile and are quickly consumed by abundant $O_i$ to form $C_iO_i$. The $C_iO_{2i}$ is observed only after (1) annealing out $C_iO_i$ by reversing Reaction 11, and (2) the released $C_i$ impurities travel and find $O_{2i}$, according to Reaction 12, ending up in a more stable complex ($E_b = 2.33$ eV). This process is limited by step 1 (annealing of $C_iO_i$), meaning that it thermally activated by the dissociation barrier of $C_iO_i$ ($E_d = 2.29$ eV). Again, this happens at temperatures below the threshold for migration of $O_i$.

The annealing of $C_iO_{2i}$ was found to follow from the capture of mobile $O_i$ impurities by $C_iO_{2i}$ as,

$$C_iO_{2i} + O_i \xrightarrow{E_m = 2.53 eV} C_iO_3,$$

whose kinetics is limited by the migration barrier of interstitial oxygen impurities ($E_m = 2.53$ eV). This picture accounts well for the annealing measurements of $C_iO_{3i}$, which was found to be thermally activated by a barrier $E_a = 2.55$ eV. Dissociation of $C_iO_{2i}$ into smaller moieties had barriers invariably above 3 eV.

The electronic properties of $C_iO_i$ and $C_iO_{2i}$ were compared by calculating their donor levels, as well as measuring their respective capture cross sections. Both theory and experiments converge well — $C_iO_i$ has a donor transition at $E_c + 0.36$ eV, only 30 meV below the analogous transition of $C_iO_{2i}$.

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