



Three carbon pairs in Si

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ABSTRACT

Carbon impurities in Si are common in floating-zone and cast-Si materials. The simplest and most discussed carbon complex is the interstitial–substitutional C_iC_s pair, which readily forms when self-interstitials are present in the material. This pair has three possible configurations, each of which is electrically active. The less common C_sC_s pair has been studied in irradiated material but has also recently been seen in as-grown C-rich cast-Si, which is commonly used to fabricate solar cells. The third pair consists of two interstitial C atoms: C_iC_i . Although its formation probability is low for several reasons, the C_iC_i pair is very stable and electrically inactive. In this contribution, we report preliminary results of first-principles calculations of these three C pairs in Si. The structures, binding energies, vibrational spectra, and electrical activity are predicted.

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1. Introduction

Carbon and C–C interactions in Si have been studied for several decades. The properties of substitutional (C_s), interstitial (C_i), and two pairs (C_iC_s and C_sC_s) have been discussed by experimentalists and theorists [1–5]. Experimental information comes from electrical (deep-level transient spectroscopy, DLTS), optical (Fourier-transform infrared absorption spectroscopy, FTIR, and photoluminescence, PL), and/or magnetic (electron paramagnetic resonance, EPR, and optically-detected magnetic resonance, ODMR) techniques.

C_s is the dominant impurity in floating-zone (FZ) Si, typically present in concentrations of the order of a few times 10^{17} cm^{-3} , close to its solubility limit at the melting temperature. Cast Si often contains above solubility concentrations of C, near 10^{18} cm^{-3} , and C pairs form during the cool-down of the material. Since the C–Si bond strength is greater than the Si–Si one, the bonding–antibonding separation is larger than the Si bandgap and C_s is electrically inactive. However, the C–Si bond length is shorter than the Si–Si one. As a result, C_s draws its four Si nearest neighbors (NNs) closer to it and thus introduces strain in the crystal.

An influx of Si self-interstitials (I_{Si}) kicks C_s out of the substitutional site and it becomes the rapidly-diffusing and electrically active C_i [1,6,7]. It traps at a range of impurities including C_s , with which it forms C_iC_s pairs [8,9].

The C_iC_s pair dissociates into C_s and C_i at 250 °C. Two configurations of the C_iC_s pair have been observed and studied theoretically. They are labeled C_iC_s -A and C_iC_s -B, and neither of them involves direct C–C bonding. A third possible configuration with

nearest-neighbor (NN) C atoms has been mentioned by Tersoff [10] but has not been observed or discussed in detail. We label it C_iC_s -NN.

C_iC_s -A is the stable configuration in the + and – charge states and has two inequivalent C atoms. It resembles C_i (a split- $\langle 100 \rangle$ interstitialcy) trapped near C_s , and has been detected by EPR, DLTS, and FTIR [1,9,11]. It has a donor (acceptor) level at $E_v + 0.09 \text{ eV}$ ($E_c - 0.17 \text{ eV}$). At low temperature, the local vibrational modes (LVMS) are at 953, 872.6, 722.4, 596.9, and 594.6 cm^{-1} .

C_iC_s -B is the stable configuration in the 0 charge state. It has two equivalent C atoms located near substitutional sites but separated by a self-interstitial [1,9,11]. An excited triplet state B^* has been seen by ODMR and B^- has been seen by EPR. The activation energy for the A-to-B transformation is 0.2 eV. C_iC_s -B has C_{1h} symmetry at low temperatures, but I_{Si} easily rotates around (or moves through) the trigonal axis above 30 K and the symmetry of the defect becomes C_{3v} [12]. C_iC_s -B has a donor (acceptor) level at $E_v + 0.07 \text{ eV}$ ($E_c - 0.11 \text{ eV}$), and a PL band with zero-phonon line at 969 meV. The fine structure in the PL band shows LVMS at 579.5 and 543.0 cm^{-1} for the ^{12}C – ^{12}C isotope combination. FTIR studies reveal LVMS at 842.4, 730.4, 640.6, 579.8, 543.3, and 540.4 cm^{-1} .

C_iC_s -NN has two equivalent C atoms aligned along a $\langle 100 \rangle$ direction sharing one substitutional site.

Leary et al. [2,3] have performed density-functional theory (DFT)-based calculations with Gaussian basis sets in the $\text{Si}_{44}\text{H}_{42}$ and $\text{Si}_{35}\text{H}_{36}$ clusters. They find that the A form is lower in energy, by 0.43, 0.35, and 0.50 eV in the +, 0, and – charge states, respectively. In the 0 charge state of the B form, the calculated LVMS (^{12}C – ^{12}C isotope combination) are 838, 715, 649, 582, 552, 543, and 532 cm^{-1} , very close to the values measured by FTIR [9].

Capaz et al. [4,5] also performed DFT-based calculations in periodic Si_{64} supercells using the local density approximation,

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plane-wave basis with a 40 Ryd cutoff, and a single k point. They found that in the 0 charge state, the B configuration is lower than the A one by 0.11 eV. The energy barrier separating the A and B configurations is only 0.13 eV. The self-interstitial between the two equivalent near-substitutional C atoms rotates about the trigonal axis with the very small 0.07 eV barrier. In the 0 charge state, the calculated LVMs for the ^{12}C – ^{12}C isotope combination are in good agreement with the measured ones in the B form (841, 716, 643, 567, 514, and 503 cm^{-1}) as well as in the A form (890, 874, 722, 567, and 557 cm^{-1}).

The C_5C_5 pair was first observed in 2 MeV e^- -irradiated FZ-Si. The formation of the defect occurs when a vacancy traps at C_iC_5 [13,14]. In cast-Si, C_5C_5 pairs exist in the as-grown material [15]. The EPR of C_5C_5 in n-Si reveals a trigonal center with spin 1/2 and approximate ab-initio Hartree-Fock calculations in H-saturated clusters predict a stable pair. The electronic energy eigenvalues suggest the presence of an acceptor level near the conduction band minimum. FTIR studies [14] show that before irradiation, the IR spectrum is dominated by the intense IR lines of C_5 (607 cm^{-1}) and V_2 (2770 cm^{-1}). After irradiation, the spectrum shows weak lines associated with C_iC_5 -A (730.4, 640.6, 579.8, 543.3, and 540.4 cm^{-1}) and C_iC_5 -B (842.4 cm^{-1}), two lines associated with an unidentified C-related defect at 527.4 and 748.7 cm^{-1} (plus two electronic transitions at 2553 and 2965 cm^{-1} , which have the same annealing behavior). These lines are assigned to C_5C_5^0 and C_5C_5^- , respectively. The lines begin to anneal out at 400 °C and disappears at 500 °C.

DFT-based calculations in the $\text{Si}_{44}\text{H}_{42}$ cluster [14] predict that C_5C_5 has an acceptor level at $E_c - 0.3 \pm 0.2$ eV. The calculated (scaled) LVMs for $^{12}\text{C}_5^{12}\text{C}_5$ show IR-active modes at 512 and 522 cm^{-1} (plus IR-inactive ones at 689 and 629 cm^{-1}) in the 0 charge state, and at 706 and 516 cm^{-1} (plus IR-inactive ones at 697 and 529 cm^{-1}) in the $-$ charge state.

The focus of the present work is on C–C pairs. We study three configurations of the C_iC_5 pair, and discuss a new pair, C_iC_i , which could form in C-rich and/or heavily irradiated Si.

2. Theoretical approach

Our first-principles approach is based on the SIESTA method [16,17]. The host crystal is represented by Si_{128} periodic supercells. The lattice constant of the perfect cell is optimized in each charge state. The defect geometries are obtained with a conjugate gradient algorithm. A $3 \times 3 \times 3$ Monkhorst and Pack [18] mesh is used to sample the Brillouin zone.

The electronic core regions are removed from the calculations using ab-initio norm-conserving pseudopotentials with the Troullier and Martins parameterization [19] in the Kleiman and Bylander form [20]. The valence regions are treated with first-principles spin-density-functional theory with the exchange-correlation potential of Ceperley and Adler [21] as parameterized by Perdew and Zunger [22] (LDA). The relative energies of some metastable structures have also been obtained at the GGA level [23]. The charge density is projected on a real-space grid with an equivalent cutoff of 150 Ryd to calculate the exchange-correlation and Hartree potentials. The basis sets for the valence states are linear combinations of numerical atomic orbitals [24,25]: double-zeta for H and C, with polarizations functions for Si.

The migration paths and activation energies for diffusion are obtained using the nudged elastic band (NEB) method [26–28]. The NEB calculations are performed in the Si_{64} supercell with a $2 \times 2 \times 2$ mesh and the RPBE form [29] of the generalized gradient approximation. This exchange-correlation functional provides [30] much more reliable activation energies for diffusion than LDA.

The vibrational spectra are obtained from a direct calculation of the force constant matrix with geometries converged down to a maximum force component smaller than 0.003 eV/Å. The dynamical matrices are diagonalized using the most abundant ^{12}C isotope.

The gap levels are evaluated using the marker method [31,32]. The perfect crystal is used as a universal marker. The position of the donor (acceptor) levels is obtained relative to top of the valence band (bottom of the conduction band). The position of any level too close to a band (< 0.10 eV or so) is unreliable.

2.1. The C_iC_5 pairs

We find three possible structures for the interstitial–substitutional pair: C_iC_5 -A, C_iC_5 -B, and C_iC_5 -NN (Figs. 1–3). The

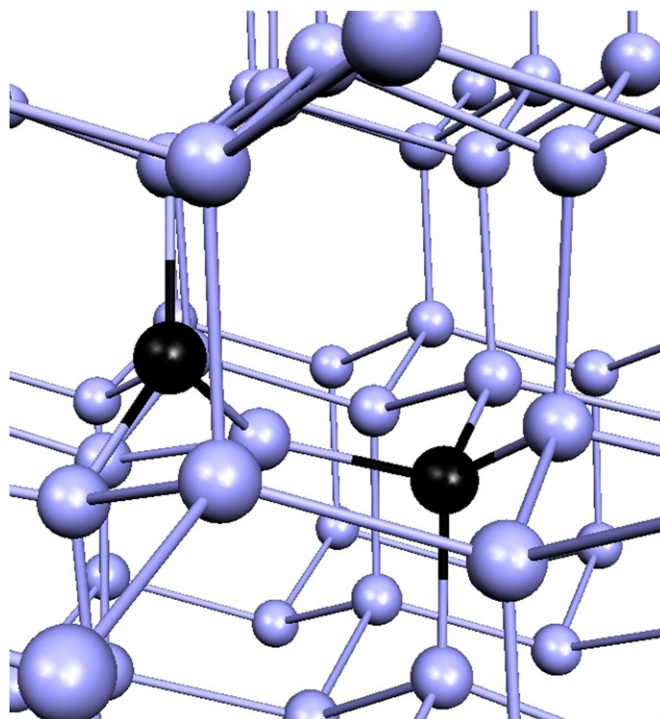


Fig. 1. C_iC_5 -A resembles isolated C_i trapped near C_5 .

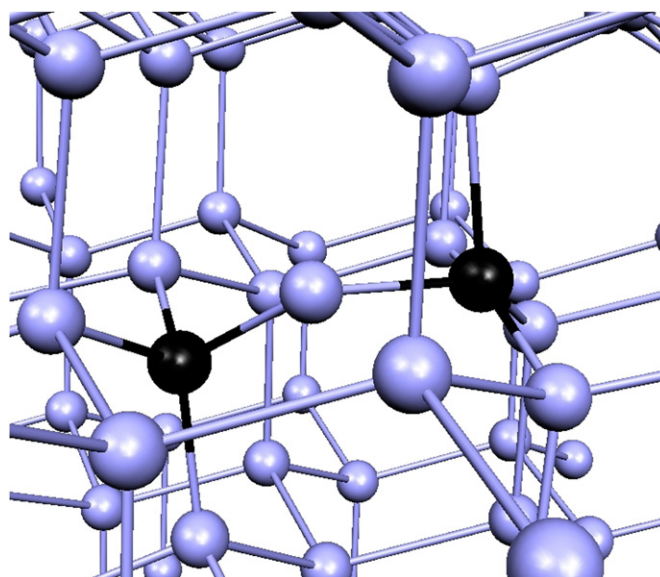


Fig. 2. C_iC_5 -B has two C's separated by I_{Si} .

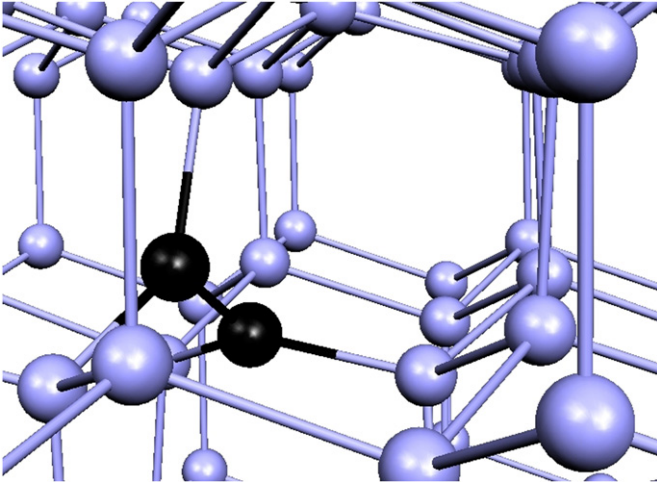


Fig. 3. C_iC_s -NN has two equivalent C's along $\langle 100 \rangle$ sharing one lattice site.

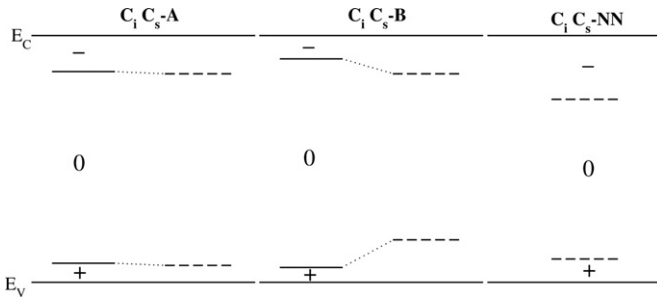


Fig. 4. Measured (solid lines) and calculated (dashed lines) gap levels of the three C_iC_s pairs.

relative energies calculated at the LDA level in the Si_{128} cell favor C_iC_s -B in all three charge states. We find that C_iC_s -A and C_iC_s -NN are higher in energy by 0.24 and 0.22 eV, respectively, in the + charge state, by 0.36 and 0.38 eV, respectively in the 0 charge state, and by 0.38 and 0.31 eV, respectively in the – charge state. This contrasts with the cluster calculations of Leary et al. [2] where the A form is found to be more stable by 0.43, 0.35, and 0.50 eV in the +, 0, and – charge state, respectively. Both predictions conflict with the experimental data, which show that the A form is the more stable one in the + and – charge states, and the B form in the 0 charge state [1,9,11]. It could be that the energy balance changes with supercell size or at the GGA level, and/or that the spurious Madelung energy term present in the + and – charge states affects the predictions.

In the 0 charge state, the binding energy of C_iC_s -B is 1.28 eV ($C_s^0 + C_i^0 \rightarrow C_iC_s-B^0 + 1.28$ eV). This number is consistent with the observed annealing temperature of 250 °C [1]. The calculated gap levels (Fig. 4) are in reasonable agreement with the experimental data.

The LVMs for the three pairs in the +, 0, and – charge states, respectively, are listed in Tables 1–3. Note that the LVM frequencies shift with the charge state.

The C_iC_s -A and C_iC_s -B pairs have been identified experimentally, but C_iC_s -NN has not. Yet, its stability is very close to that of C_iC_s -A. The reason for this is that when C_i approaches C_s , it traps in the A or B form, and then must overcome a barrier larger than the dissociation energy of the pair to realize the NN form. Indeed, NEB calculation of the C_iC_s -NN to C_iC_s -A and C_iC_s -NN to C_iC_s -B transitions involve barriers larger than the dissociation energy of the pair: about 3.21 and 2.23 eV, respectively, as one C atom needs to break two C–Si bonds to achieve the conversion. Both

Table 1

Calculated LVMs (cm^{-1}) of $^{12}C_i^{12}C_s$ -A in the +, 0, and – charge states. The measured [9] LVMs associated with this structure are at 953, 872.6, 722.4, 596.9, and 594.6 cm^{-1} .

+	0	–
913	917	953
908	912	813
712	710	693
599	598	660
592	591	594

Table 2

Calculated LVMs (cm^{-1}) of $^{12}C_i^{12}C_s$ -B in the +, 0, and – charge states. The measured [9] LVMs associated with this structure are at 842.4, 730.4, 640.6, 579.8, 543.3, and 540.4 cm^{-1} .

+	0	–
802	805	809
693	704	714
653	663	682
569	567	600
563	563	570
546	549	557

Table 3

Calculated LVMs (cm^{-1}) of $^{12}C_i^{12}C_s$ -NN in the +, 0, and – charge states. The C–C stretch is not IR active. No IR lines have been associated with this configuration.

+	0	–
1119	1181	1149
821	810	823
566	806	570
	580	

values are higher than the binding energy of the pair. Note that our calculations predict that the B form is the most stable one in all three charge states.

2.2. The C_sC_s pair

The C_sC_s pair only forms in irradiated material when C_iC_s traps a vacancy ($C_iC_s^0 + V^0 \rightarrow C_sC_s^0 + 3.28$ eV) or in as-grown cast Si which contains above solubility concentrations of C ($C_s^0 + C_s^0 \rightarrow C_sC_s^0 - 1.70$ eV). The C_sC_s pair has an acceptor level close to the conduction band, $E_c - 0.07$ eV. The donor level is almost resonant with the top of the valence band. The C–C bond length in the 0 (–) charge state is 1.708 Å (1.714 Å), considerably longer than the ~ 1.53 Å typical of C–C bond lengths in molecules.

In the 0 charge state, the LVMs are at 655, 591, 554, and 537 cm^{-1} . The latter is IR-active and close to the 527.4 cm^{-1} line reported for $C_sC_s^0$ [14].

2.3. The C_iC_i pair

The formation of C_iC_i is a low-probability event because the concentration of C_i is always much lower than that of C_s and thus the rapidly-diffusing C_i has a much higher probability of trapping at C_s before encountering another C_i , and because C_i is in the + (–) charge state in p- (n-) type Si resulting in long-range repulsion. The C_iC_i defect has never been reported in the literature. However, it is remarkably stable: $C_i^0 + C_i^0 \rightarrow C_iC_i^0 + 2.71$ eV. The defect forms if two C_i 's at neighboring interstitial sites move

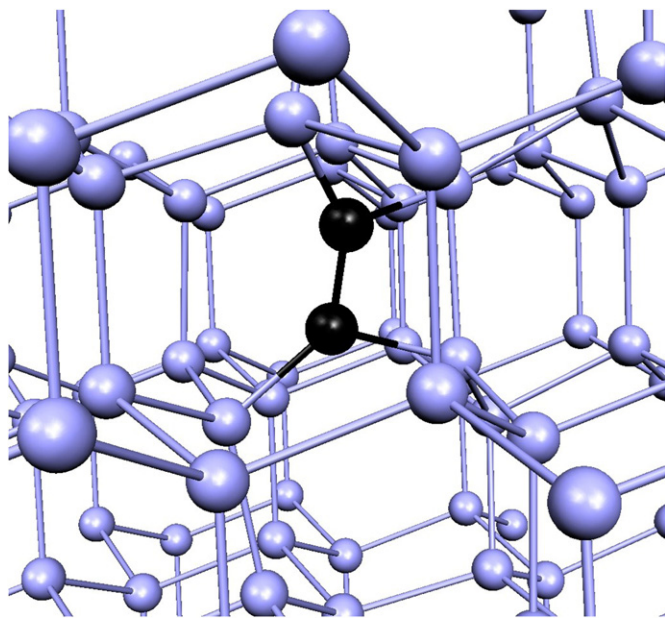


Fig. 5. Unlikely but very stable and electrically inactive C_iC_i pair in Si.

toward each other to form a C–C bond (almost along $\langle 211 \rangle$ Fig. 5).

The donor (acceptor) level is below the top (above the bottom) of the valence (conduction) band, and C_iC_i is electrically inactive and always in the 0 charge state. The LVMS are at 1424, 878, 813, 658, and 568 cm^{-1} , respectively. The latter mode involves almost only Si motion.

3. Summary and discussion

We have studied five CC pairs in Si in the Si_{128} supercells. The structures, relative energies, gap levels, and vibrational spectra in all the possible charge states are predicted. The barriers between various metastable configurations are still being calculated. The binding energies, gap levels, and LVM frequencies are consistent with the experimental data when such data are available. Our preliminary results are summarized as follows.

Two of the C_iC_s pairs are well known (C_iC_s -A and C_iC_s -B) but the third configuration (C_iC_s -NN) is described here for the first

time. Its stability is very close to that of C_iC_s -A but it has not been observed experimentally. The reason is that when C_i approaches C_s , it traps in the A or B form, and then must overcome a barrier larger than the dissociation energy of the pair to realize the NN form. Our calculations predict that the B form is the most stable one in all three charge states.

A new defect is predicted, the C_iC_i pair. Its formation probability is low, but it is very stable and electrically inactive.

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