

The carbon-substitutional-carbon-interstitial (C_sC_i) defect pair in silicon from hybrid functional calculations

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Highlights

- HSE06 functional predicted charge-state controlled metastability of C_sC_i defect.
- PBE functional predicted no form of charge-state controlled metastability.
- Calculated binding energy indicates the defect complex exists as a bound complex.

Abstract

Using both the Perdew-Burke-Ernzerhof (PBE) functional and the hybrid functional of Heyd-Scuseria-Ernzerhof (HSE06), the metastability of the carbon-substitutional-carbon-interstitial (C_sC_i) defect in silicon has been investigated within density functional theory using the two experimentally proposed configurations of the defect. While the PBE functional predicted the defect complex to have both donor and acceptor levels, it did not predict any form of charge-state controlled metastability as was observed experimentally. In the case of HSE06 functional, the defect was found to exhibit charge-state controlled metastability in the 0 and -1 charge states with no metastability predicted for +1 charge state. The calculated binding energies for the neutral charge state indicate that the defect is a stable bound defect complex.

Keywords: (A: Defects, B: Semiconductors, C: Metastability, D: Density Functional Theory)

1. Introduction

Defect studies, both theoretical and experimental, in semiconductors have mainly focussed on stable defects. Stable defects are defects that are known to exist in only one stable atomic configuration over a wide range of experimental and operational conditions. These defects are usually easy to detect and characterize experimentally because they usually possess distinct characteristics or signatures that are easily discernable. These defects usually have only one atomic configuration, which also makes them easy to model theoretically. On the hand, other studies, mainly experimental, have reported on defects that may exist in one or more stable atomic configuration depending on the experimental or operational conditions. These defects are known as metastable (bistable) defects [1–6]. The reason why metastable defects pose a challenge when one attempts to model them theoretically can be attributed to the fact that the two configurations of the defect being close energy thus the formation energy difference will be small. This has been mentioned by Song *et al.*[5] that “*It should be a real challenge to a theorist to duplicate these results and provide a good physical picture for the driving forces and the effect of the charge state*” and hence the motivation for this study. Technologically, it is important to understand defect metastability because, the presence of metastable defects in a device may lead to erratic behaviour, as in the case of the thermal donors in silicon [7] as well as the source of light induced degradation of hydrogenated amorphous silicon [8].

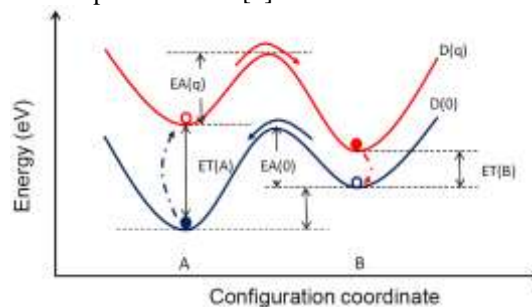


Figure 1: Configuration coordinate diagram of a metastable defect and the neutral and a charge state q . $EA(q)$ and $EA(0)$ are the defect migration energies and $ET(A)$ and $ET(B)$ are the transformation energies.

Unlike stable defects, metastable defects are defects or defect complexes with different atomic configurations (say configuration A and configuration B) in different charge states where one configuration, configuration A is the minimum energy configuration in one charge state and configuration B is the stable configuration in the other charge state (see Figure 1). Defects exhibiting such characteristics have been observed experimentally using Deep-Level Transient Spectroscopy (DLTS) experiments where DLTS peaks appear or disappear when a spectrum is recorded under reverse or forward bias conditions after annealing[1–6]. Notable examples of experimentally observed metastable defects include; the substitutional boron vacancy complex in silicon (B_sV) whose metastability had been associated to different DLTS peaks by different experiments[1,9], the interstitial-iron-substitutional-aluminium (Fe_iAl_s) pair in silicon[6], the substitutional europium vacancy complex in GaN ($Eu_{Ga}V_N$)[10] and the carbon-substitutional-carbon-interstitial (C_sC_i) defect in silicon[3–5]. The carbon-substitutional-carbon-interstitial (C_sC_i) defect in silicon has similar metastable characteristics as the Fe_iAl_s pair in p -type silicon.[6] In the case of the Fe_iAl_s pair, it has been experimentally suggested that, its metastability results from the change in Coulomb interaction between the deep donors, in this case the iron (Fe) interstitial, and a negatively charged substitutional acceptor (in this case the substitutional aluminium (Al)). It is this Coulomb interaction that causes a change in the relative stability of the interstitial Fe in the nearest and next-nearest neighbour position w.r.t the substitutional acceptor.[6]

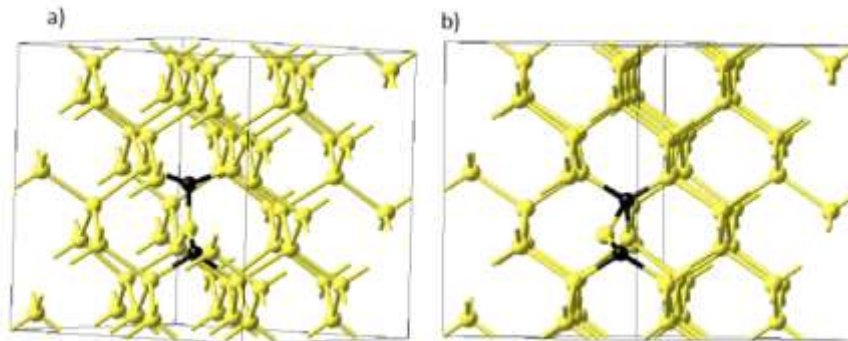


Figure 2: Figure showing the two configurations of the C_sC_i defect in silicon. a) is Configuration A and b) is Configuration B.

In the case of the C_sC_i defect in silicon, Song *et al.*[3–5] proposed the defect complex to exist in two stable (minimum energy) configurations namely: Configuration A, where the defect is formed by one substitutional carbon atom sitting next to a carbon “interstitialcy” in which a carbon-silicon “molecule” shares a lattice site (See Fig 1) and Configuration B, where the defect is formed by two substitutional carbon atoms with one silicon atom squeezed in between them and is slightly displaced from the bond centre along the $\langle 111 \rangle$ direction [3–5] (See Fig. 2). In their study, Configuration A was found to be stable in the singly charge states (+1 and –1) and Configuration B was stable in the neutral charge state. Each of these configurations was then observed to change/transform to the other configuration by a simple bond-switching transformation. According to [5], the metastability of this defects was found to results from a molecular bond switching between two configuration that are very close in energy.

In this study the exchange-correlation (XC) within the density functional theory (DFT) formalism has been approximated using both the generalized gradient approximation (GGA) as well as HSE06[11,12] hybrid functional to investigate the experimentally observed metastability of C_sC_i defect in silicon. The calculated formation energies at various charged states as well as the thermodynamic charge transition levels have been used to draw conclusions as to whether this defect is metastable or not. In addition we propose a possible configuration coordinate (CC) diagram and compare it to the experimentally observed CC diagram[5]. Standard DFT using GGA or local density approximation (LDA) is known to severely underestimate the band gap of semiconductors however hybrid functionals have been shown to remedy the band gap under estimation issue[13]. The success of hybrid functionals in predicting the defect properties has been underscored in several studies including[14–19] however, hybrid functionals are also known to fail in describing defect properties in some cases[20–22] hence the reason for using both GGA and HSE06. We compare how the two XC functionals predict the metastability of the defect complex in relation to the experimental observations. As earlier mentioned, even though metastable defects have attracted the attention of experiments, theoretical investigations have mainly focussed on stable defects and defect complexes. Very few theoretical studies have attempted to investigate defect metastability[23,24].

2. Computational details

All DFT calculations were done based on the generalized Kohn-Sham approach[25] and the projector-augmented wave (PAW) method[26,27] as implemented in the Vienna *Ab initio* Simulation Package (VASP) code.[28] We have used the Heyd-Scuseria-Ernzerhof (HSE06)[12,29] hybrid functional with Perdew-Burke-Ernzerhof (PBE)[30] generalized gradient approximation (GGA) pseudopotentials. The optimised unit cell of silicon was obtained using a kinetic energy cut-off of 500 eV, the Brillouin zone was sampled with a $8 \times 8 \times 8$ Monkhorst-Pack[31] grid of k -points from which the band gap of silicon was found to be 0.65 eV using PBE and 1.13 eV using HSE06, The HSE06 result is in agreement with both previous *ab initio* studies [32,13] as well as experiment [33]. For defect calculations, we have used 64 atom Si supercells with a kinetic energy cut-off of 500 eV, the Brillouin zone was sampled with a $2 \times 2 \times 2$ Monkhorst-Pack[31] grid of k -points. Similar supercell sizes have been used to investigate defects complexes in Ge[21,22] and Si[34,35]. The defects were allowed to relax to an accuracy of 10^{-6} eV and the finite supercell correction was done according to the scheme of Freysoldt *et al.*[36,37]. The defect formation energies were calculated according to the Zhang and Northup formalism.[38] Within this formalism, the formation energy of the defect in this case, the $C_s C_i$ at charge state q is given by,

$$E_{C_s C_i}^q = E_{\text{tot}}(C_s C_i^q) - E_{\text{tot}}(\text{Si}) + \mu_{\text{Si}} - 2\mu_{\text{C}} + q(E_{\text{F}} - E_{\text{V}}) + E_{\text{Corr}}^{\text{FNV}} \quad (1.0)$$

where, $E_{\text{tot}}(C_s C_i^q)$ is the total energy of the $C_s C_i$ defect supercell at charge state q , $E_{\text{tot}}(\text{Si})$ is the total energy of the pristine Si supercell, μ_{Si} and μ_{C} are the chemical potentials for Si and C respectively, E_{F} is the Fermi level, referenced to the valence-band maximum (VBM) E_{V} and $E_{\text{Corr}}^{\text{FNV}}$ is the Freysoldt, Neugebauer, and Van de Walle (FNV) correction term that accounts both for the potential alignment between the charged defect and bulk a point far from the defect and charge corrections in a supercell of finite size[36,37,39]. The FNV scheme explicitly uses the electrostatic potential obtained from DFT calculations to obtain an electrostatics model. This correction is given by

$$E_{\text{Corr}}^{\text{FNV}} = E_{\text{iso}} - E_{\text{per}} - q\Delta V_{q/b}$$

where, E_{iso} is the self-energy of the isolated charge distribution, E_{per} the electrostatic energy of the system subject to periodic boundary conditions and $q\Delta V_{q/b}$ is the potential alignment term. This scheme has been shown to be more suited for charged defects within a dielectric medium and the formation energies obtained within scheme have been found to be independent of the adopted charge model for a localized defect charge within a supercell[39].

3. Results and discussions

The binding energy of a defect pair (complex) is the energy needed to dissociate the defect pair into its constituent defects. The binding energy of this defect complex was obtained using relation $E_{\text{binding}} = E_{C_s} + E_{C_i} - E_{C_s C_i}$ where E_{C_s} , E_{C_i} and $E_{C_s C_i}$ are the formation energies of interstitial carbon (C_i), substitutional carbon (C_s) and the $C_s C_i$ defect complex, respectively. All the computed binding energies using both PBE and HSE06 were greater than 0 eV but less than 0.1 eV. Small but positive binding energies imply that the defect complex exists as a stable bound complex that does not dissociate into its constituent point defects.

From the calculated formation energies (See Table 1), PBE functional predicted the minimum energy configuration to be Configuration B in all charge states. HSE06 on the other hand predicted Configuration A as the minimum energy configuration in the -1 charge state while configuration B was the minimum energy configuration in the neutral and +1 charge states. This can also be seen in Fig 2. Since the defect has different minimum energy configurations in different charge states, the defect complex is said to exhibit charge-state controlled metastability in the -1 and neutral (0) charge states. This predicted charge-state controlled metastability is partly consistent with experimental observations where metastability was observed in -1 and 0 charge states[3–5]. No charge-state controlled metastability was predicted for the 0 and +1 charge state even though experimentally the defect exhibited metastability for these charge states too [3–5].

Table 1: Calculated defect formation energies of configurations A and B of the C_sC_i defect in silicon and the difference in formation energies dE at different charge states and thermodynamic transition levels w.r.t VBM. All energies reported in the table are in eV.

Functional	Configuration	charge state			thermodynamic transitions	
		-1	0	1	(-1/0)	(0/+1)
PBE	A	4.64	4.22	4.18	0.42	
	B	4.59	4.18	4.12	0.43	0.06
	dE	0.05	0.04	0.06		
HSE06	A	5.54	4.76	4.95	0.79	
	B	5.58	4.72	4.79	0.86	
	dE	0.04	0.04	0.16		

On plotting the formation energy of the two configurations at different values of the Fermi level in different charge states (see Figure 3), PBE predicted donor and acceptor levels at $E_v+0.06$ eV and $E_c-0.22$ eV for configuration A and only an acceptor level at $E_c-0.23$ eV for configuration B. HSE06 on the other hand, predicted the defect to have only the -1/0 thermodynamic transitions for both configuration A and B at $E_c-0.27$ eV for configuration A and $E_c-0.35$ eV for configuration B. This prediction is partly consistent with experimental results however, as earlier mentioned, experimentally this defect complex was observed to have the 0/+ transition levels too[3–5]. As seen in Fig. 2, In the case of HSE06, when E_{Fermi} is close to E_v , where E_v is the valence band maximum, configuration B is the minimum energy configuration, this is consistent with experimental observations of [5]. The defect then remains in this configuration up to a Fermi level of 0.9 eV above E_v where the minimum energy configuration switches to configuration A as E_{Fermi} approaches the conduction band minimum E_c . This is also consistent with experimental observations[5]. This shows that it is possible to switch the minimum energy configuration from A to B and vice versa by changing the charge state accordingly and this can be done experimentally by applying a suitable bias either forward or reverse to the sample or theoretically by shifting the Fermi level position either towards E_v or E_c .

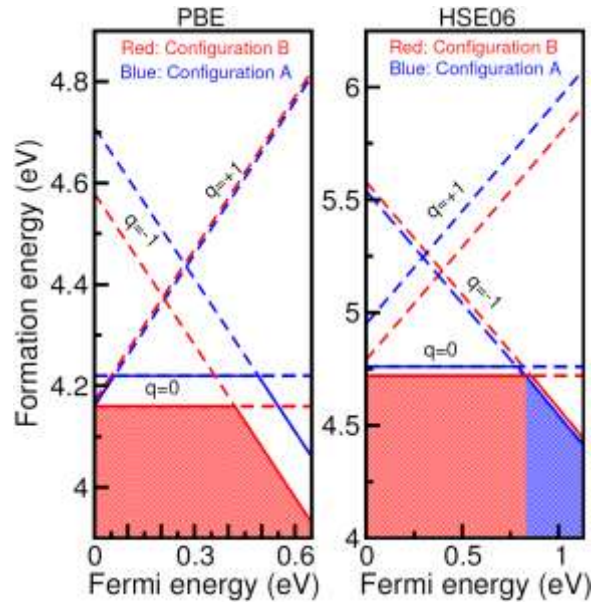


Figure 3: PBE and HSE06 calculated formation energies for configurations A and B at various charge states as function of the Fermi level. Solid lines indicate the stable charge state and the shaded regions indicate the regions where each configuration is the minimum energy configuration.

In order for two defects in the same charge state to have similar occupations, their formation energy difference ought to be at least approximately kT at room temperature however, if the formation energy difference between the two configurations is approximately $3kT$ (approximately 0.1 eV at room temperature) or greater, then the occupation ratio of the two configurations will be 1:10 assuming that there is no degeneracy. This results in one configuration being dominant over the other. From the calculated formation energies, the formation energy difference in the -1 and 0 charge states, in the case of HSE06, was 0.04 eV which is less than kT at room temperature making it possible to observe peaks associated with both configurations A and B from DLTS measurements since the two defects will have similar occupations. This is also consistent with experimental observations[3–5]. The same can be said for the case of PBE since the formation energy difference is also less than kT and room temperature, however as seen in Figure 3, PBE predicts the configuration B as the minimum energy configuration in all the charge states. PBE only predicted the minimum energy configuration for neutral charge state correctly.

From the HSE06 results we the proposed a possible CC diagram and compared to the experiment of [5]. As can be seen in Figure 4, HSE06 gave a consistent description with the experimental observation. The differences in energies can be attributed to DFT being a 0K calculation.

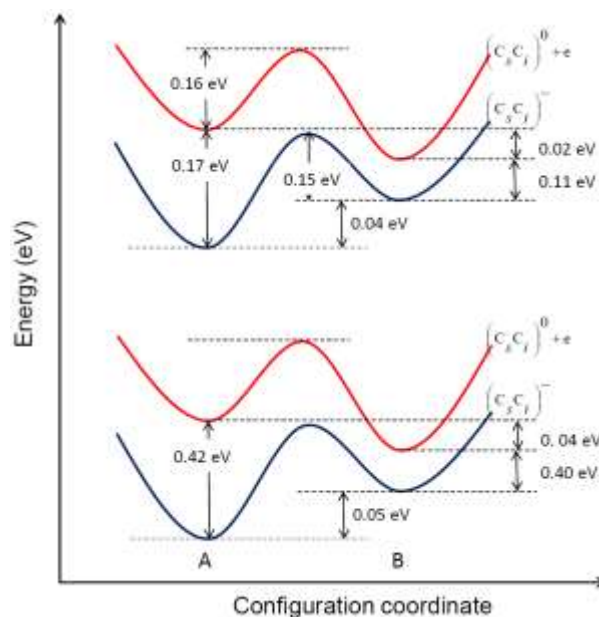


Figure 4: Experimental (top panel) and computed (bottom panel) configuration coordinate diagram the acceptor state of the CsCi defect in silicon. Experimental results have been derived from[5]

4. Conclusion

Using PBE and the HSE06 hybrid functional within the DFT formalism, we have investigated the charge-state controlled metastability of the $C_s C_i$ defect in silicon using experimentally proposed configurations of the defect. We report evidence of charge-state controlled metastability of the defect in the -1 and 0 charge states with no metastability observed in the +1 charge state for the case of HSE06 and no metastability for the case of PBE. Although the predicted metastability is consistent with experimental observations, experimentally this defect is metastable in +1 charge state too.

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