An ab-initio study of the metastability of the boron-vacancy complex in silicon

Cecil N M Ouma and Walter E Meyer
Department of Physics, University of Pretoria, Private Bag X20, Pretoria, 0002, South Africa

E-mail: walter.meyer@up.ac.za

Abstract. Using the experimentally proposed model of the C centre in silicon (Si), we have calculated the electronic properties of the C centre defect in Si using Perdew-Burke-Ernzerhof (PBE) with a Γ-point (PBE- Γ) as well as a 2×2×2 k-mesh (PBE-2×2×2) sampled Brillouin-zone (BZ). The choice of BZ sampling was found to significantly influence the calculated defect properties. PBE-2×2×2 did not predict any metastability of the C centre, PBE-Γ predicted charge-state controlled metastability of the C centre under both bias on and bias off conditions. The C1 and C2 configurations, in which the boron-vacancy pairs are in the nearest- and next-nearest-neighbour positions, have been predicted as the metastable configurations of the C centre in Si.

1. Introduction

The semiconductor electronics industry has evolved from macro to micro and recently to nano electronics. As the circuits become more miniaturized and the packing density becomes larger, there is need for more understanding of the fundamental properties of the semiconductors in use. Other semiconductors including GaAs, GaN, AlGaN, graphene, boron nitrine and ZnO are also currently intensively being studied both experimentally and theoretically as possible alternatives to silicon (Si). However, interfacing these semiconductors with the Si drive electronics is still costly and problematic.[1]

Defects can be beneficial or detrimental in the functionality of semiconductor devices, and need to be taken into account in device design. A fundamental understanding of these defects and their properties is essential in defect engineering. Most defects in semiconductors are known to be stable in one specific configuration is all charge states. However, the same defects may occur in more than one configuration, at either of the charge states. These types of defects are referred to as metastable defects.[2–5] In silicon, several metastable defects have been experimentally observed, some of these include; the FeAl pair[3], the CsCi defect pair[4,5] and the boron-vacancy (B-V) pair, also known as the C centre,[2] among others.

The C centre has been observed using deep-level transient spectroscopy (DLTS) by Chantre[2] in ultra-fast-quenched boron-doped Si to be metastable. In the study, Chantre observed that this defect centre introduced two deep donor-hole traps at 0.50 eV and 0.36 eV above the valence band maximum (VBM). These two donor-hole traps were associated to the next-nearest- and nearest-neighbour B-V pairs in silicon respectively.

Theoretical studies have also been done on both the isolated B_{Si} and V_{Si} as well as the B-V pair (complex) in Si.[6–8] However a survey of the available literature on the theoretical studies on B-V

complex (C centre) in Si reveals that these studies have only been on impurity- or vacancy-mediated diffusion in Si.[6,7] None of these studies have investigated the metastability of the C centre defect in Si.

Although density functional theory (DFT) has been used to study defects in semiconductors,[9–11] it has been shown that DFT inaccurately predicts defect thermodynamic transition levels among other properties[12–15]. These failures of DFT stem mainly from the approximations made to the exchange-correlation (XC) functional. The local density approximation (LDA)[16,17] and the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA),[18] are the most commonly used approximations of the XC functionals. Although several attempts have been made to remedy some of the failures of DFT, [12,14,19–22] standard DFT (using LDA or GGA) can still be used to investigate some defect properties in semiconductors but with additional corrections.[9,23]

2. Computational details

We have used PBE form of GGA within standard DFT We have used the projector-augmented wave (PAW) method,[24,25] as implemented in the VASP code.[26,27] The unit cell was optimized using an energy cutoff of 600 eV and a Γ centred 8×8×8 Monkhorst-Pack grid of *k*–points using PBE. We obtained a lattice constant of 5.45 Å. From this, supercells consisting of 64 silicon atoms were constructed. PBE defect calculations were done using the 64 silicon atoms supercell with a kinetic energy cutoff of 600 eV, Methfessel-Paxton (MP) smearing of 0.02 eV, and a Γ-point (hereto referred as PBE-Γ) as well as a Γ cantered 2×2×2 Monkhorst-Pack grid of *k*–points (hereto referred as PBE-2×2×2) to sample the Brillouin zone (BZ). Band gaps of 0.65 eV (PBE-2×2×2) and 0.50 eV (PBE-Γ) were obtained. The experimental band gap of silicon is 1.12 eV.[28] While the Γ-point sampling of the BZ is often regarded as the simplest scheme of sampling the BZ, Puska *et al.*[29] using LDA XC functionals showed that in some cases (e.g. vacancy in silicon), this sampling scheme gives a correct qualitative description of the defect compared to a 2×2×2 *k*–points sampled BZ.

We considered two configurations of C centre namely; C1, where the silicon vacancy (V_{Si}) is at the nearest-neighbour position w.r.t. the substitutional boron (B_{Si}), and C2 in which V_{Si} is in the next-nearest-neighbour position w.r.t. the B_{Si} as suggested by Chantre[2] (see Figure 1). Formation energies of the defects were calculated using the Zhang and Northrup formalism[30] i.e., the formation energy of the C centre in silicon at charge state q is

$$E^{f,q}(BV) = E_{D,q} - E_p + 2\mu_{Si} - \mu_B + q(E_F + E_V + \Delta V) \tag{1}$$

Where $E_{D,q}$ is the total energy of the defect supercell at charge state q, E_p is the total energy of the pristine 64 atoms silicon supercell, μ_{Si} and μ_B are the chemical potentials for Si and B respectively, E_F is the Fermi level, E_V is the valence band maximum (VBM) and ΔV is the potential alignment term. For the charged supercells, a jellium charge compensating background of opposite sign was used, as implemented in the VASP code. Monopole correction[23] was done on the total energies and potential alignment between the pristine and the defect supercell was done using the technique of ref [9]. The thermodynamic transition level, ε, for q' and q charge sates was obtained as

$$\varepsilon(q/q') = \frac{E^{f,q'}(BV) - E^{f,q}(BV)}{q - q'}, \tag{2}$$

giving the Fermi energy at which the formation energies of the defect in the two charge states are equal.

 ISBN: 978-0-620-70714-5

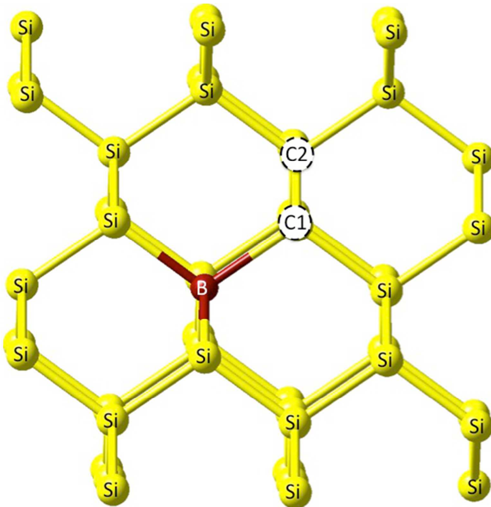

Figure 1. The V_{Si} position for the C1 and C2 configurations of the C centre in silicon.

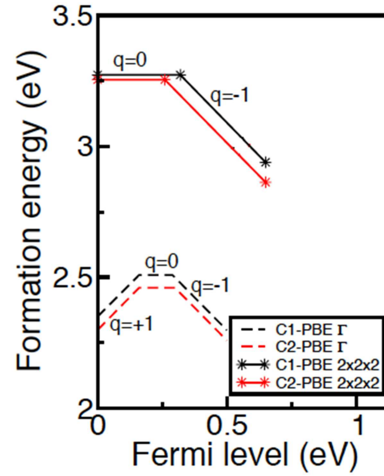

Figure 2. Figure showing the thermodynamic transition levels for the C1 and C2 configurations of the C centre in silicon.

2.1. *V_{Si} defect in silicon*

The isolated vacancy in silicon, V_{Si} has been extensively studied via *ab initio* LDA within DFT by Puska *et al.*[29] we have calculated both the formation energies at various charge states using equation 3.2 (Table 1) and the thermodynamic charge transition levels using equation 3.3. Our calculated formation energies, for both PBE-Γ and PBE-2×2×2, are in good agreement with those of Puska *et al.*[29] Although the calculated thermodynamic transition levels are in good agreement with those calculated by Puska *et al.*,[29] they are not consistent with the experimentally reported values[31], which report no defect levels associated with donor states only and with acceptor states.

2.2. *B_{Si} defect in silicon*

Most of the theoretical studies in literature have investigated interstitial boron in silicon (B_i). Substitutional boron in silicon (B_{Si}), is a shallow acceptor in silicon. Similar to case of V_{Si}, we calculated the formation energies of B_{Si} defect in various charge states (see Table 1) from which its thermodynamic transition levels were determine (see Figure 2). Formation energy calculated

Table 1. Calculated formation energies in eV at various charge states (figures in bold indicate minimum energy configurations).

Defect	Functional	-1	0	1
V-Si	PBE-2×2×2	3.01	2.80	2.83
	Ref [29]-2×2×2	3.68	3.42	3.72
	PBE-Γ	2.85	2.43	2.1q
	Ref [29]-Γ	3.56	2.86	2.51
B-Si	PBE-2×2×2	1.33	0.75	0.68
	PBE-Γ	0.16	0.22	0.33
C1	PBE-2×2×2	3.59	3.27	3.41
	PBE-Γ	3.29	2.69	**2.29**
C2	PBE-2×2×2	**3.51**	**3.26**	**3.32**
	PBE-Γ	**2.94**	**2.64**	2.48

Table 2. Calculated thermodynamic transition levels in eV for the defects referenced to the valence band edge.

Defect	Functional	0/–	+/0
V-Si	PBE-2×2×2	0.20	--
	Ref [29]-2×2×2	0.26	--
	PBE-Γ	0.42	0.32
	Ref [29]-Γ	0.70	0.35
	Experiment[31]	--	0.05
B-SI	PBE-2×2×2	0.57	0.07
	PBE-Γ	--	--
	Experiment[32]	0.05	--
C1	PBE-2×2×2	0.32	--
	PBE-Γ	0.28	0.23
	Experiment[2]	--	0.36
C2	PBE-2×2×2	0.26	--
	PBE-Γ	0.30	0.21
	Experiment[2]	--	0.50

according to PBE-Γ was the lowest, while PBE-2×2×2 yielded the highest formation energy. Only PBE-2×2×2 predicted thermodynamic transition levels at $E_V + 0.07$eV and $E_V + 0.57$eV respectively. It is evident that PBE-Γ gives the incorrect description of B_{Si}. However, its important to mention that experimentally, B_{Si} has only an acceptor level at 0.045 eV.[32] Since B_{Si} is a shallow acceptor in silicon, no alignment term for the defect levels was used in calculating the formation energies for its charged states. This is because the alignment of shallow defect levels is still the subject of on-going debate.[23,33,34] Furthermore, due to the large hydrogenic orbitals of the shallow donor, it is not clear that the super cell chosen in this study is large enough.

2.3. C centre in silicon

B_{Si} is a shallow accepter in silicon, while V_{Si} is known to be highly mobile in silicon. When these two defects interact they form the C centre defect in silicon. We have calculated the formation energies (Table 1) at various charge states as well as the thermodynamic transition levels (Table 2 and Figure 2) for two different configurations of the C centre. The main aim of this study is to investigate the metastability of the C centre and if the metastability is charge-state controlled. From our study we found that both the formation energy and the thermodynamic transition levels are dependent on the position of vacancy in the silicon lattice (configuration dependent). This is in agreement with what was observed experimentally.[2] In that study, Chantre [2] experimentally observed two donor-hole traps that were associated to next-nearest- and nearest-neighbour configurations of the C centre. C2 was found to be the most stable configuration for all the charge states using PBE-2×2×2. For the case of PBE-Γ, C2 was the most stable configuration for the -1 and neutral charge state while C1 was the most stable configuration for the +1 charge state.

2.3.1. Metastability of the C centre and comparison to experiment. Chantre[2] using DLTS experiments posited that the C centre in Si was configurationally bistable. From that experiment, it was observed that the C centre had donor levels at $E_V + 0.54$ eV and $E_V + 0.36$ eV that were associated with two DLTS peaks. Chantre[2] labeled these peaks H_1 and H_2 respectively. The same experiment identified the H_1 and H_2 peaks as associated with the next-nearest- and nearest-neighbour B-V pairs, respectively. In our study, as mentioned in section 2. we refer to the nearest- and next-nearest-neighbour configurations as C1 and C2 respectively.

In *p*-type material, under zero bias (referred to as *bias off* by Chantre[2]), the Fermi level is close to the valence band edge (E_V), i.e. $E_F \approx E_V$. This leads to defects emitting electrons (i.e. filled with holes). Under reverse bias (referred to as *bias on* by Chantre[2]), the Fermi level in the depletion region of a Schottky diode is close to the conduction band edge (E_C), i.e. $E_F \approx E_C$. This leads to defects capturing electrons (i.e. emitting holes). Since it was experimentally observed that the emission rates of the H_1 and H_2 peaks did not depend on the electric field, it was concluded that these two peaks correspond to donor levels,[2] e.g. $+/0$.

The annealing by Chantre[2] was performed at approximately 300 K, which leads to a value of kT of 0.026 eV. This implies that, for the occupation of two defect configurations to differ significantly, the difference in their formation energies should be at least approximately kT. A difference in formation energy of approximately $3kT$ ($\approx$ 0.1 eV) or greater would lead to the ratio of occupation of the two configurations to be 1:10 or greater (assuming no degeneracy). This means that, experimentally, one level will dominate.

As seen in Figure 2, PBE-2×2×2 does not predict a $+/0$ thermodynamic transition level. Ignoring this, we still went ahead to analyze whether there was any sign of metastability predicted by PBE-2×2×2, using the $q = 0$ and $q = -1$ charge states. For the $0/-$ thermodynamic transition, the C1 transition level is deeper than the C2 transition level w.r.t. E_V. This implies that, in a DLTS experiment, C1 will emit at a lower rate than the C2, and therefore the emission by the C1 configuration will be observed at a higher temperature than that of the C2.

Under *bias off*, $q = 0$, the C2 configuration was the most stable configuration of the C centre. The formation energy difference between the two configurations was 0.018 eV, which is less than $3kT$ at 300 K. This implies that both the C1 and C2 defect levels will be observed since they will have roughly similar occupation probabilities. This is not consistent with what was reported by Chantre[2], who observed only one dominant peak. Furthermore, the PBE-2×2×2 prediction here implies that the dominant peak, the C2 in this case, is likely to be observed at lower temperatures, which is also not consistent with the reported experimental results.[2]

Under *bias on*, $q = -1$, the C2 configuration is still the most stable configuration. The formation energy difference between C1 and C2 configurations is 0.075 eV. This implies that the C2 configuration, which gives rise to the lower temperature DLTS peak, is predicted to be more dominant. This is also not consistent with what was reported by Chantre[2], who observed both peaks at approximately equal heights under these conditions.

PBE-2×2×2 thus predicts variation in peak heights of the H_1 and H_2 peaks after annealing under different bias conditions. However, the relative (temperature) positions of the peaks and their relative heights do not agree with experiment.[2]

PBE-Γ predicted both the $+/0$ and $0/-$ thermodynamic transition levels (see Figure 2). In both cases, the transition level for the C2 configuration is closer to E_V compared to that of the C1 configuration. This implies that there will be faster (hole) emission by C2 and hence, C2 is likely to be observed at lower temperature compared to the C1. This differs from the experimental observation by Chantre[2], who associated the higher temperature peak (H_1) with the C2 configuration.

Under *bias off*, $q = +1$ and PBE-Γ predicted the C1 as the most stable configuration of the C centre. The formation energy difference between the C1 and C2 configurations was 0.190 eV, which is greater than $3k$T at 300 K. This implies that, under these conditions, only the C1 configuration will be occupied and hence experimentally observable. As discussed earlier, the C1 configuration leads to a DLTS peak at higher temperature. This agrees with the experimental observations of Chantre[2], who observed the higher temperature DLTS peak under *zero bias*.

Under *bias on*, $q = 0$ and C2 is the most stable configuration. The formation energy difference between the two configurations is only 0.049 eV, which is about $2kT$ at 300 K implying that both the C1 and C2 configurations will be experimentally observable, with the occupation of the C2 configuration (at lower temperature) being significantly higher than that of the C1 (ignoring the effects of degeneracy). If degeneracy is taken into account, the occupation of C2 would be increased by a factor 2.5. Chantre[2] experimentally observed both the H_1 and H_2 peaks, with the H_1 (at higher temperature) having a much lower peak height, as a shoulder of the $H(0.44)$.

PBE-Γ predicts some metastability, which agrees with the experimental observations[2], but not with the identification of the defect configurations.

3. Conclusions

We used DFT with GGA functionals to investigate the metastability and other properties of the C centre (B-V complex) in silicon and compared our results to the experimentally observed values. In addition, we have also investigated the properties of isolated defects that form the B-V defect (V_{Si} and B_{Si}). We have compared how the choice of *k*-points used in sampling the BZ influenced the predicted defect properties of V_{Si}, B_{Si} and the C centre in silicon.

Our predicted properties of V_{Si} defect in silicon were consistent with those predicted by Puska *et al.*[29] The choice of BZ sampling significantly influenced the predicted defect properties. We found that the PBE functional using Γ-point sampling (PBE- Γ) gave a better qualititative description of the defect compared to the PBE functional using a 2×2×2 *k*-mesh (PBE-2×2×2). For B_{Si}, only PBE-2×2×2 predicted thermodynamic transition levels in the band gap.

Although PBE-Γ predicted some form of charge-state controlled metastability of the C centre that was consistent with experimental observations, the identity of the defect configurations was not

consistent with other experimental observations. PBE-2×2×2 only predicted variations in peak heights under different bias conditions that were not consistent with the experimental observations.

Acknowledgement
This work is based on the research supported in part by the National Research Foundation of South Africa (Grant specific unique reference number (UID) 76938) Opinions, findings and conclusions or recommendations are that of the authors, and that the NRF accepts no liability whatsoever in this regard. The authors would also like to acknowledge Prof. Nithaya Chetty for helpful discussions.

References

[1] Kenyon A J 2005 *Semicond. Sci. Technol.* **20** R65–84
[2] Chantre A 1985 *Phys. Rev.* B **32** 3687–94
[3] Chantre A and Bois D 1985 *Phys. Rev.* B **31**
[4] Song W, Benson W and Watkins G D 1990 *Phys. Rev.* B **42**
[5] Song L W, Benson B W and Watkins G D 1987 *Appl. Phys. Lett.* **51** 1155
[6] Nichols C, Van de Walle C and Pantelides S 1989 *Phys. Rev.* B **40** 5484–96
[7] Windl W and Stumpf R 2008 *Mater. Sci. Eng.* B **155** 198–201
[8] B., Cowren N. E., F., K. T. F. Janssen, G. F. A. van de Walle D J G 1990 *Phys. Rev. Lett.* **65** 2434–7
[9] Van de Walle C G 2004 *J. Appl. Phys.* **95** 3851
[10] Van de Walle C G and Janotti A 2011 *Phys. Status Solidi* **248** 19–27
[11] Stampfl C, Van de Walle C, Vogel D, Krüger P and Pollmann J 2000 *Phys. Rev.* B **61** R7846–9
[12] Komsa H-P and Pasquarello A 2011 *Phys. Rev.* B **84** 075207
[13] Komsa H-P, Broqvist P and Pasquarello A 2010 *Phys. Rev.* B **81** 205118
[14] Parker W D, Wilkins J W and Hennig R G 2011 *Phys. Status Solidi* **248** 267–74
[15] Lany S and Zunger A 2010 *Phys. Rev.* B **81** 113201
[16] Ceperley D M 1980 *Phys. Rev. Lett.* **45** 566–9
[17] Wang Y and Perdew J 1991 *Phys. Rev.* B **44** 13298–307
[18] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865–8
[19] Oba F, Togo A and Tanaka I 2008 *Phys. Rev.* B **77** 245202
[20] Alkauskas A, Broqvist P and Pasquarello A 2011 *Phys. Status Solidi* **248** 775–89
[21] Shang H, Li Z and Yang J 2011 *J. Chem. Phys.* **135** 034110
[22] Ouma C N M, Mapelu M Z, Makau N W, Amolo G O and Maezono R 2012 *Phys. Rev. B* **86** 104115
[23] Lany S and Zunger A 2008 *Phys. Rev.* B **78** 235104
[24] Blöchl P E 1994 *Phys. Rev. B* **50** 17953–79
[25] Kresse G and Joubert D 1999 *Phys. Rev.* B **59** 1758–75
[26] Kresse G and Hafner J 1993 *Phys. Rev.* B **48** 13115–8
[27] Kresse G and Furthmüller J 1996 *Comp. Mat. Sci.* **6** 15–50
[28] Streetman B G and Banerjee S 2000 *Solid state electronic devices* vol 4 (Prentice Hall New Jersey)
[29] Puska M, Pöykkö S, Pesola M and Nieminen R 1998 *Phys. Rev.* B **58** 1318–25
[30] Zhang S and Northrup J 1991 *Phys. Rev. Lett.* **67** 2339–42
[31] Watkins G D and Pantelides S T 1986 *Gordon Breach, New York* 147
[32] Morin F and Maita J 1954 *Phys. Rev.* **96** 28–35
[33] Freysoldt C, Neugebauer J and Van de Walle C G 2011 *Phys. Status Solidi* **248** 1067–76
[34] Freysoldt C, Neugebauer J and Van de Walle C 2009 *Phys. Rev. Lett.* **102** 016402