

Light induced degradation in B doped Cz-Si solar cells

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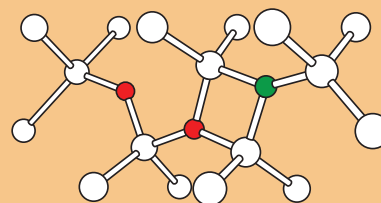
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We analyse the formation energy of interstitial boron (B_i) and the properties of the defect resulting from its association with an oxygen dimer (B_iO_{2i}) to evaluate the possibility that it may be the slow-forming centre responsible for the light-induced degradation of B-doped Si solar cells. However, we find that the formation energy of B_i is too high, and therefore its concentration is negligible. Moreover, we find that the lowest energy form of B_iO_{2i} is a shallow donor, and the deep donor form is high in energy.



Lowest energy structure of the B_iO_{2i} defect.

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1 Introduction The efficiency of $p-n^+$ solar cells fabricated from boron-doped Czochralski (Cz)-grown silicon is severely compromised by light-induced degradation, which can cause up to a 10% (relative) reduction of its value [1]. This degradation is caused by at least two defects that act as recombination centres for electrons and holes, one forming in a timescale of minutes and the other in a timescale of hours.

One of the models for the formation of the slow-forming centre identified it with the substitutional boron–oxygen di-interstitial defect (B_sO_{2i}) [1, 2].

This assignment explained (i) the linear dependence of the concentration of the slow-forming centre on the substitutional boron (B_s) concentration and quadratic dependence on the interstitial oxygen (O_i) concentration [1], (ii) the fact that its formation is triggered by illumination (or minority carrier injection) [2], and (iii) its formation kinetics [3]. The key point was the excitation of the oxygen dimers (O_{2i}^+), which in the presence of an over-equilibrium concentration of minority charge carriers would undergo a Bourgoin–Corbett migration mechanism, being trapped at substitutional boron.

However, the B_sO_{2i} model has been unable to explain why, in B–P co-doped samples, the degradation (characterised by the saturated value of the increment in the reciprocal lifetime and the rate constant) depends on the hole density (p) rather than on the boron concentration $[B]$ [4, 5]. Moreover, the determination of the concentration dependence of the neutral state of O_{2i} on $[O_i]$ in p - and n -type Cz-Si and the absence for a signature of O_{2i}^{2+} suggest that O_{2i} does not exist in the double positive charge state [6], a requirement for the proposed light-induced migration O_{2i} mechanism [2]. This led Voronkov and Falster to introduce another model [5], where the formation of the slow-forming centre results from a photo induced transformation of a latent complex consisting of a boron interstitial and an oxygen dimer (B_iO_{2i}), in the positive charge state. According to that model, the density of recombination centres is proportional to the concentrations of O_{2i} and B_i^+ .

In this paper, we use density functional theory to estimate the fraction of B_i^+ in equilibrium with B_s^- , showing that the density of the former is negligible. Further, we show that even if B_iO_{2i} was formed, would not be an efficient recombination centre.

2 Method The calculations were carried out using a density functional code within the local spin density approximation, as implemented in the AImpro code (see Refs. [7, 8] for more details). Core states are treated using the dual space separable pseudopotentials by Hartwigssen et al. [9]. Valence states are expanded over a set of atom-centred Cartesian–Gaussian functions. These consist of (4, 12, 12) independent s-, p-, and d-like functions centred on each Si atom. For O and B we use a total of 40 and 22 Gaussian basis functions, respectively. In the reciprocal space, a plane-wave basis set with a cutoff energy of 200 Ry was used. This method has been successful in previous studies of boron–oxygen defects in Si [10].

Unless otherwise specified, the calculations presented in Section 3 were performed using Si₅₁₂ supercells, using one Monkhorst and Pack (MP) special **k**-point [11]. The calculations in Section 4 were performed using Si₂₁₆ supercells, and the integration over the Brillouin zone was performed with resource to an MP-2³ special **k**-point scheme [12].

In order to assess the convergence of formation energies and levels, additional calculations were performed using supercells with up to 1728–1729 atoms. Calculations with more than 1000 atoms were performed using basis set filtration [12–14], with four filtration functions per atom and a filtration radius of 12 atomic units. This algorithm leads to formation energies accurate to ≈ 1 meV (see Fig. 1) while using ≈ 7 times fewer basis functions.

3 Formation energies In thermal equilibrium, the solid solubility of a defect is determined by the condition minimising the Gibbs free energy,

$$C_X = C_s \exp(-E_f[X]/kT), \quad (1)$$

where C_X is the concentration of the defect X, $C_s \gg C_X$ is the number of available sites, $E_f[X]$ is the defect formation

energy at temperature T and k is the Boltzmann constant. The formation energy of a defect X in charge state q , at $T=0$, can be calculated using

$$E_f[D^q] = E_{\text{sup}}^n(X^q) - \sum_i m_i \mu_i + qE_F, \quad (2)$$

where $E_{\text{sup}}^n(X)$ is the energy of a supercell of n Si atom sites, with the defect X, m_i and μ_i are the number of atoms and the chemical potential of species i , respectively, and E_F is the Fermi level.

The difference between the formation energies (E_f) of interstitial and substitutional boron, both in the neutral charge state, is

$$\begin{aligned} E_f(B_i) - E_f(B_s) &= E_{\text{sup}}(B_i) - \mu_B - n\mu_{\text{Si}} \\ &\quad - [E_{\text{sup}}(B_s) - \mu_B - (n-1)\mu_{\text{Si}}] \\ &= E_{\text{sup}}(B_i) - E_{\text{sup}}(B_s) - \mu_{\text{Si}}. \end{aligned}$$

We obtain $E_f(B_i) - E_f(B_s) = 2.5$ eV. As B_s is a shallow acceptor, the convergence of its energy with the supercell size is slow (see, e.g. the discussion in Ref. [15]). Having this into consideration, we have performed calculations in supercells of different sizes (n ; Fig. 1a). Calculations with up to $n=1000$ were performed with a regular basis set. In addition, we have performed calculations with up to $n=1728$ using the basis set filtration algorithm described in Refs. [12–14]. The trend of the results in Fig. 1 shows that $E_f(B_i) - E_f(B_s)$ is converged within 0.05 eV for $n \geq 512$ atoms, tending to 2.55 eV when $1/n \rightarrow 0$.

For the charged defects B_i^+ and B_s^- ,

$$E_f(B_i^+) = E_f(B_i) + [E_F - B_i^{(0/+)}], \quad (3)$$

$$E_f(B_s^-) = E_f(B_s) + [B_s^{(-/0)} - E_F], \quad (4)$$

where E_F is the Fermi level and $E_X^{(q/q+1)}$ is the charge transition level between charge states q and $q+1$. We note that Eq. (4) is only valid when the Fermi level is below the $B_i^{(-/+)} level, and Eq. (3) is only valid when the Fermi level is above the $B_s^{(-/0)}$ level. Then$

$$\begin{aligned} E_f(B_i^+) - E_f(B_s^-) &= E_{\text{sup}}(B_i) - E_{\text{sup}}(B_s) - \mu_{\text{Si}} \\ &\quad - B_i^{(0/+)} - B_s^{(-/0)} + 2E_F. \end{aligned} \quad (5)$$

We obtain the defect transition levels $E_X^{(q/q+1)}$ using the semi-empirical marker method, since these are usually more accurate than those calculated directly from the formation energies [16], due to a partial cancellation of the systematic errors introduced by the bandgap underestimation and by spurious supercell charge distribution effects. The marker defect should be chosen amongst well-known defects with transition levels in the same region of the bandgap. Thus, we have used sulphur (S), a deep donor [17], as a marker for $B_i^{(0/+)}$, and the valence band (the bulk 0/+ level) as a

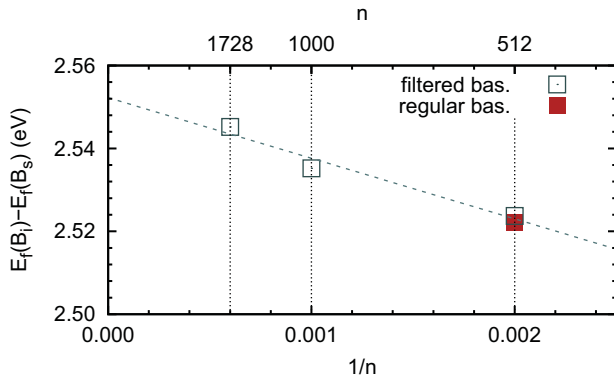


Figure 1 (online color at: www.pss-a.com) Convergence of the calculated formation energy with the supercell size. n represents the number of atoms in the perfect supercell. The full square represents a calculation using the regular basis functions. The open squares represent the calculations performed using basis set filtration (see Section 2).

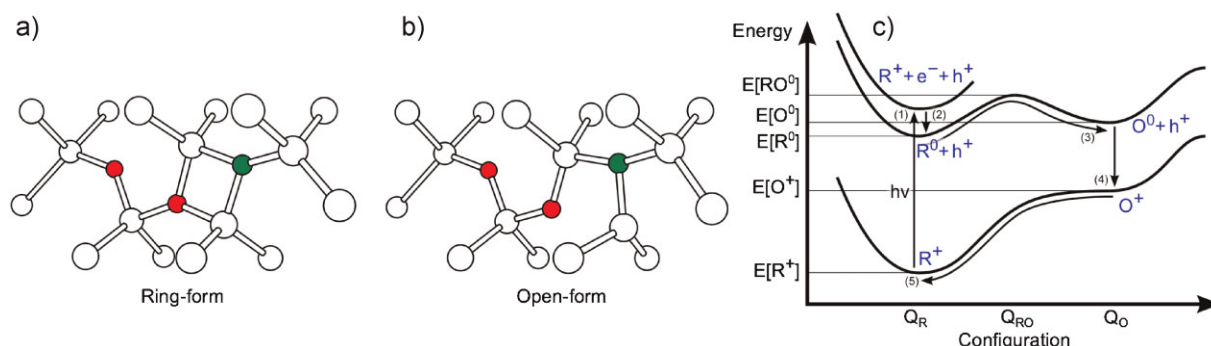


Figure 2 (online color at: www.pss-a.com) Lowest energy structures of B_iO_{2i} in silicon (a) and (b), along with their configuration coordinate diagram (c). In (a) we depict the ground state structure (referred as ring-form) for the neutral and positive charge states, whereas in (b) we depict the second most stable structure (referred as open-form). Oxygen and boron are coloured in red and green, respectively. The configurational coordinate diagram curves are schematic and only the minima and saddle point energies were calculated by first-principles. e^- and h^+ represent free electrons in the conduction band bottom and valence band top, respectively.

marker for $B_s^{(-/0)}$. This result, obtained with a 1000 atom supercell, is converged within less than 0.01 eV with the supercell size.¹ We obtain $B_s(-/0) = E_v + 0.0$ eV, and $B_i(0/+) = E_c - 0.1$ eV, in excellent agreement with the experimental values, which are respectively $E_v + 0.045$ eV [18] and $E_c - 0.13$ eV [19]. Using the occupancy levels calculated with the marker method in Eq. (5), we obtain the difference between the formation energies of the charged defects $E_f(B_i^+) - E_f(B_s^-) = 2.7 - E_g + 2(E_F - E_v)$ eV, where E_g is the bandgap energy, for $B_s^{(-/0)} < E_F < B_i^{(-/+)}$. At mid-gap, the difference between the formation energies of these two defects is 2.7 eV, about 1 eV larger than the difference between the formation energies of the vacancy-oxygen defect and the interstitial oxygen defect calculated using the same method (1.7 eV).

4 The B_iO_{2i} defect Now we assess the B_iO_{2i} complex in Si as a contender to explain the light-induced degradation of the solar cells. From a total of 16 defect structures tested in different charge states, we arrived at two particularly stable forms which we label as *ring-form* (R) and *open-form* (O), respectively. This labelling becomes clear by looking at Fig. 2a and b, where they are depicted. While the R-form has an over-coordinated oxygen atom and all other species adopt their usual coordination, the O-form has an under-coordinated Si atom (connected to boron), and the O atoms are now bound to two Si neighbours each. The energy difference between these structures in the neutral charge state is $E[O^0] - E[R^0] = 0.10$ eV. Previously reported structures for B_iO_{2i} complexes, namely $\{B_iO_{2i}\}_1$ and $\{B_iO_{2i}\}_2$ from Ref. [20] were found metastable with respect to the ring-form by 0.38 and 0.35 eV, respectively.

Figure 2c depicts a configuration coordinate diagram for the R- and O-forms. The energy curves are shown to guide

the eye as only the minima and seven structures separating both forms, including saddle points, were calculated by first principles. The latter were obtained by employing the nudged elastic band method as detailed elsewhere [21]. The energy barrier to break a Si–O bond separating the O-form from the R-form was estimated as $E[RO^0] - E[R^0] = 0.31$ eV. Although the process involves breaking a Si–O bond, its small barrier mirrors the fact that the oxygen atom goes from an high-energy over-coordinated configuration to a twofold coordinated structure.

Over-coordinated oxygen in Si usually is a source of donor activity. We looked at the positive charge state of these defects and found that the R-form is now considerably more stable than the O-form, $E[O^+] - E[R^+] = 0.64$ eV. This is depicted in the lower energy curve of the configuration coordinate diagram, that is, it is assumed that the host crystal is p-type, so that the lowest energy state is positive. The positively charged O-form is marginally stable and an almost vanishing barrier of about 5 meV prevents the defect from relaxing spontaneously to the R-form.

We estimate the position of a donor level with respect to the valence band top by comparing the ionisation energy of defective cells with the same calculation for a bulk supercell. Accordingly, the ionisation energy of a cell with the R-form of B_iO_{2i} is 1.02 eV smaller than that of a pristine supercell, meaning that this defect has a donor level at $E_v + 1.02$ eV (or $E_c - 0.15$ eV if we consider $E_g = 1.17$ eV for the band gap of Si at cryogenic temperatures). This also means that $E[R^0 + h^+] - E[R^+] = 1.02$ eV in the coordinate diagram of Fig. 2. Similarly, for the O-form we calculated $E[O^0 + h^+] - E[O^+] = 0.48$ eV. We note that while the R-form has a relatively *shallow* donor state typical of an oxygen aggregate with an over-coordinated O atom, the O-form has a deep donor state near mid-gap arising from the under-coordinated Si dangling bond. Looking at Fig. 2 it is clear that individual R- and O-forms hardly account for the properties of an efficient recombination centre. Firstly,

¹ To avoid spurious filling effects, the total energy calculations used to obtain $B_s(-/0) - E_v$ were performed at the Γ -point of the Brillouin zone – see Ref. [15].

the R-form is definitively a shallow-donor-like defect, similar to shallow thermal donors in heat-treated O-rich Si [22]. This clashes with estimates from injection-level dependent carrier-lifetime measurements that place the minority carrier trap between $E_v + 0.35$ eV and $E_c - 0.45$ eV [23]. Secondly, although the O-form has a level compatible with a deep recombination centre, the donor state is marginally stable and at room-temperature (even in dark) this defect should not occur in p-type Si.

An efficient recombination defect must have sufficiently large capture cross sections for both electrons and holes. This condition could in principle be filled by the deep O-form state, but as we pointed out above, the structure is not stable. In analogy to the B_iO_{2i} model by Du et al. [24] and in contrast to the usual fixed-level Shockley-Read-Hall recombination, B_iO_{2i} could show a defect-bistability-mediated carrier recombination mechanism. This works like a mill of carriers and can be explained by the five steps depicted in Fig. 2. We start with the positively charged ground state R^+ . In Step 1, light is absorbed and promotes an electron-hole pair in the material ($R^+ + e^- + h^+$). In Step 2, previously promoted minority electrons are captured by the donor state of B_iO_{2i} ($R^0 + h^+$). In Step 3, the defect transforms to the $O^0 + h^+$ state through the 0.31 eV barrier. In Step 4, the O-form captures a majority hole at the deep donor level (O^+), and finally, in Step 5 relaxes back to the ground state R^+ . Unfortunately, there are serious difficulties with this picture. The first is that it is limited by the barrier separating neutral R- and O-forms. Secondly, the energy released by the capture of the electron (Step 2) is not larger than the barrier height, so that it can not assist the subsequent transformation. Thirdly, the neutral O-form is metastable and this limits the concentration of defects available to capture a hole. Transformation processes are usually 3–4 orders of magnitude faster than capture processes, so that the back-transformation towards the $R^0 + h^+$ state should be faster than the capture mechanism.

5 Conclusions We found that the B_iO_{2i} defect does not explain, to the current understanding, the light-induced recombination.

First, based on the calculation of the formation energies, we find that $[B_i]$ is negligible. According to the model by Voronkov and Falster [5], B_i is in equilibrium with boron-interstitial clusters. Thus, $[B_i]/[B_s] = \exp\{-[E_f(B_i^+) - E_f(B_s^-)]/kT\}$, but $E_f(B_i^+) - E_f(B_s^-) = 2.7$ eV for a Fermi level at mid-gap. For a representative boron concentration of 10^{16} cm^{-3} , $[B_i] < 10^{-10} \text{ cm}^{-3}$ at 250 °C, hence there are just too few B_i defects present to account for the recombination activity.

In addition, the lowest energy form of the B_iO_{2i} defect is a shallow donor. Although there is also a metastable deep donor form, the O-form, the transformation barrier is

~ 0.3 eV. Thus, the defect properties are hardly consistent with an efficient recombination centre.

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