Degradation of Boron-Doped Czochralski-Grown Silicon Solar Cells

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The formation mechanism and properties of the boron-oxygen center responsible for the degradation of Czochralski-grown Si(B) solar cells during operation is investigated using density functional calculations. We find that boron traps an oxygen dimer to form a bistable defect with a donor level in the upper half of the band gap. The activation energy for its dissociation is found to be 1.2 eV. The formation of the defect from mobile oxygen dimers, which are shown to migrate by a Bourgoin mechanism under minority carrier injection, has a calculated activation energy of 0.3 eV. These energies and the dependence of the generation rate of the recombination center on boron concentration are in good agreement with observations.

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Silicon solar cells have important uses as alternative terrestrial electricity sources and for supplying electric power in space satellites. Monocrystalline n^+-p silicon cells with external efficiencies as high as 24.7% [1] have been fabricated using silicon with low oxygen concentration, grown via the float-zone (FZ) technique. The relatively high cost of FZ-Si spurred interest in using cells made using Czochralski-grown silicon (Cz-Si) which contains around 2 orders of magnitude more oxygen ($\sim 10^{17}$ cm^{-3} or larger). These cells have efficiencies of around 19–20% [2]. Early Cz-Si boron-doped solar cells were found to suffer considerable degradation due to the light-induced dissociation of Fe-B pairs, which results in the loss of the $E_c - 0.29$ eV donor level of Fe-B and the formation of a level at $E_v + 0.4$ eV due to interstitial Fe. Electrons and holes can efficiently recombine at this level [3–5], resulting in a significant drop in carrier lifetime and hence cell efficiency. Even iron-free but boron doped Cz-Si cells show an economically significant relative efficiency reduction of about one tenth when illuminated by solar radiation [6,7] and a similar efficiency loss when electrons (minority carriers) are injected into the system via the application of an external voltage [7]. This degradation has been attributed to carrier recombination at a boron-oxygen center [8–10]. This boron-oxygen defect is the concern of the present work.

Minority-carrier-lifetime spectroscopic studies have shown that the concentration of this recombination center is proportional to [B] [9–11] and $[\mathrm{O}]^2$ [10,12], suggesting a complex of a single boron atom with a pair of oxygen atoms, contrary to earlier results which found a stronger oxygen dependence [11]. Hydrogen may be introduced during processing steps such as etching. By measuring the passivation of substitutional boron by hydrogen, as a function of distance from the crystal surface it has been shown that etching introduces hydrogen only to a depth ~ 10 μm [13]. Since the lifetime degradation has been shown to be due to a bulk property of the material [9], the involvement of hydrogen introduced by such processing can be excluded. The generation of the defect involves two processes [14]: a fast process which will not be discussed here and a slower process activated by an energy $E_A^{\mathrm{gen}} = 0.37$ eV [12,14]. For the slower process, its generation rate per center is proportional to $[\mathrm{B}]^2$ [15,16] and to the light intensity up to a critical value of just 10^{-2} suns after which it saturates [10]. The defect anneals out in the dark at ~ 200 °C with an activation energy of 1.3 eV [10,15,16].

Schmidt *et al.* [10,12,14] have put forward a model where interstitial oxygen dimers O_{2i}, already present in the material, are converted to some fast diffusing form they call $\mathrm{O}_{2i}^{\star}$. E_A^{gen} then corresponds to the diffusion barrier of $\mathrm{O}_{2i}^{\star}$ which migrates quickly through the material until it is trapped by B_s forming the recombination center $\mathrm{B}_s\mathrm{O}_{2i}$. The center has so far evaded detection by deep level transient capacitance spectroscopy but injection-level dependent carrier-lifetime measurements place the level at which the minority carrier trapping occurs at between $E_v + 0.35$ and $E_c - 0.45$ eV [9]. Using advanced lifetime spectroscopy the level was pinned down to $E_c - 0.41$ eV [17].

The aim of this Letter is to investigate models of the center and its formation mechanism using the AIMPRO spin-polarized density functional theory code. Here pseudopotential calculations were carried out using sets of s, p, and d Cartesian Gaussian basis functions. Supercells equal in size to bulk Si cells of 64, 144, and

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216 atoms were used. The Brillouin zone was sampled using a Monkhorst-Pack k-point sampling scheme of density $2 \times 2 \times 2$ [18]. These parameters were found to be sufficient for convergence. Electrical levels were examined by comparing the ionization energy of the defect with those of known donors and double donors such as C_i and S_2 [19]. The Kohn-Sham band structures were also studied. Diffusion barriers were calculated by following the procedure used in Ref. [20]. More details of the method have been given in earlier applications to boron defects [21,22] and oxygen dimers in Si [20,23].

Our calculations reveal that the substitutional B atom which has trapped an oxygen dimer, B_sO_{2i}, exhibits a charge-driven bistability. The two most stable structures (shown in Fig. 1) are labeled $B_sO_{2i}^{sq}$ and $B_sO_{2i}^{st}$. The first involves over-coordinated oxygen atoms as indeed found for other oxygen defects such as C_iO_i [24], B_iO_i [22], and thermal donors [23,25,26]. $B_sO_{2i}^{sq}$ is the more stable configuration in the single positive charge state by 0.4 eV while $B_sO_{2i}^{st}$ is the more stable when neutral, also by 0.4 eV. $B_sO_{2i}^{sq}$ has a $(0/+)$ level in the upper half of the band gap which we place between $E_c - 0.1$ and $E_c - 0.3$ eV when the defect geometry is constrained to lie in the square form. The barrier for conversion of neutral $B_sO_{2i}^{sq}$ into $B_sO_{2i}^{st}$ is 0.78 eV and thus, when $B_sO_{2i}^{+sq}$ has trapped a minority-carrier electron at any temperature too low for this barrier to be surmounted, it remains in the square form and is able to trap a hole returning to its stable charge state. It thus acts as a recombination center and the relevant defect level must then be that of B_sO_{2i} frozen in the square form, reported above. This differs from the thermodynamic $(0/+)$ level which would correspond to a change in configuration from $B_sO_{2i}^{+sq}$ to $B_sO_{2i}^{0st}$ upon minority carrier capture. This level is 0.4 eV lower and around $E_c - 0.5$ to $E_c - 0.7$ eV. The thermodynamic level controls the equilibrium concentration of charged defects and could be measured in a Hall-effect experiment. The wave function of the donor state is localized mainly on the silicon atoms indicated by arrows in Fig. 1. It is largely p-orbital-like in character. The calculated level is close to that observed as being responsible for the minority-carrier-lifetime degradation, given that errors in the calculation are around 0.2 eV, and its donor character is consistent with its large electron-capture cross section which is about 10 times that of the hole-capture cross section [17].

We now discuss the formation of the B_sO_{2i} defect. The diffusion energy of the most common oxygen defect, a single interstitial O_i is 2.5 eV [27] and thus these defects are immobile at room temperature. O_i is bound in the form of oxygen dimers by $E_B \sim 0.3$ eV [28]. It is likely that oxygen dimers are formed and frozen into the wafers during heat treatments to remove thermal donors. The dimer has been observed by infrared absorption and its concentration is found to depend upon $[O_i]^2$ [28] which would in turn lead to the quadratic dependence upon oxygen concentration for the concentration of lifetime-degrading complexes, observed experimentally [10,12]. In the neutral charge state dimers take the staggered form shown in Fig. 2 and are calculated to diffuse with an energy of about 1.3 eV [20,29], confirmed by our present calculations. The saddle point for their migration is close to a square configuration O_{2i}^{sq} shown in Fig. 2. This configuration has a deep filled level which is empty for O_{2i}^{++} and suggests that the dimer can be a bistable defect. In fact, the total energy of O_{2i}^{++sq} lies 0.6 eV below that of O_{2i}^{++st} while O_{2i}^{st} is more stable than O_{2i}^{sq} in the single positive and neutral charge state by 0.4 and 1.3 eV, respectively. The first and second donor levels of the dimer are at about $E_c - 1.0$ and $E_c - 0.6$ eV, respectively. Since the first donor level lies below the second, the defect has negative U with the occupancy $(0/++)$ level lying at $\sim E_v + 0.4$ eV. In p-type Si, with the Fermi level below this level, the dimer would be present as O_{2i}^{++sq}. However, if the first donor level lay very close to or beneath E_v, then hole capture would be less efficient and only a fraction of the dimers would be found in this charge state.

It is instructive to examine the energy profile for the diffusion of O_{2i}^{++} (Fig. 3). The saddle point for conversion

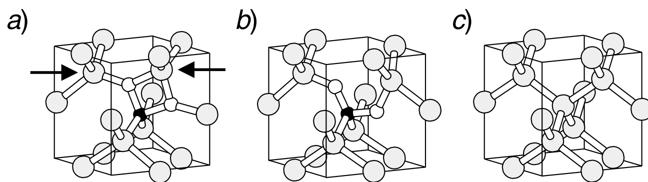

FIG. 1. The structure of the two most stable forms of B_sO_{2i}. Large gray balls represent silicon, small white are oxygen and small black are boron. The square form of B_sO_{2i}, $B_sO_{2i}^{sq}$ (structure a above) is the most stable form in the single positive charge state and is metastable in the neutral charge state. The staggered form, $B_sO_{2i}^{st}$ (structure b above) is the most stable form in the neutral charge state. An equivalent piece of perfect bulk silicon is shown (structure c above) to aid the reader. The arrows indicate the Si atoms on which the largest fraction of the donor-state wave function resides.

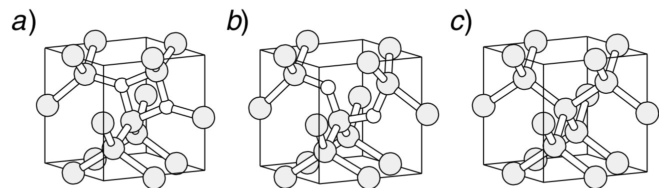

FIG. 2. The structures of the oxygen dimer. O_{2i}^{sq} (structure a above) is the stable form of the dimer in the double positive charge state. The stable form of the dimer in the neutral and single positive charge states is labeled O_{2i}^{st} (structure b above). Also shown is a piece of equivalent bulk material (structure c). As before, gray balls represent Si and small white ones represent O.

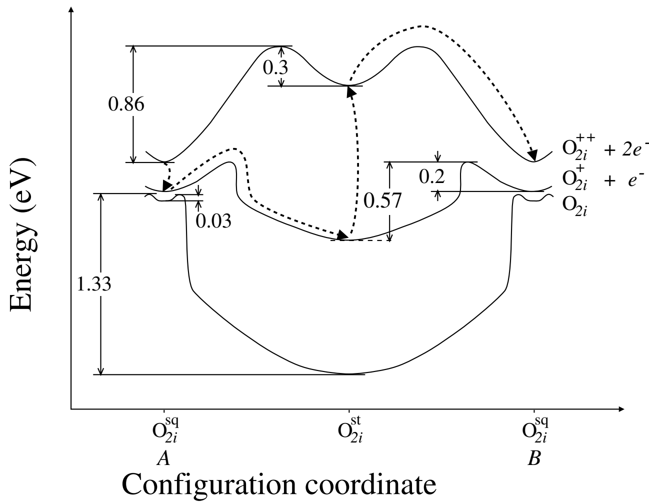

FIG. 3. A configuration-coordinate diagram for the oxygen dimer. Arrows show the proposed thermally assisted Bourgoin diffusion mechanism with a thermal barrier of 0.3 eV. O_{2i}^{++sq} at *A* first captures a photogenerated or injected electron and, after overcoming a 0.2 eV barrier, changes its configuration to O_{2i}^{+sq}. It then traps a hole becoming O_{2i}^{++sq}, and executes a diffusion jump to O_{2i}^{++sq} at *B* after overcoming a thermal barrier of 0.3 eV.

from the square to the staggered form lies between these forms and has energy 0.86 eV higher than O_{2i}^{++sq} while the barrier to move O_{2i}^{++} out of the metastable staggered configuration is only 0.3 eV. Hence in *p*-type material the oxygen dimer will have a migration barrier of 0.86 eV and is thus almost immobile at room temperature. Under photon irradiation or minority-carrier injection however, if O_{2i}^{++sq} traps an electron, becoming O_{2i}^{+}, it moves with a barrier of just 0.2 eV to the staggered configuration. The defect would then emit the electron becoming O_{2i}^{++st}. From here it has to overcome a barrier of 0.3 eV to move to another square configuration where the migration process could repeat. This *Bourgoin* mechanism [30] leads to a dimer-diffusion energy of only 0.3 eV as shown schematically in Fig. 3. Under these conditions the migration of the dimer could proceed at room temperature. This migration energy is close to the observed barrier of 0.37 eV for the formation of the B_sO_{2i} center under minority carrier injection [12].

The mobile oxygen dimers will be trapped both by oxygen atoms forming O_{3i}^{++} and by B_s^- forming $B_sO_{2i}^{+}$. The capture radius in the latter process will be considerably enhanced by the Coulomb attraction between B_s^- and O_{2i}^{++}. The binding energy between B_s^- and O_{2i}^{++} can be estimated from the change in energy when B_s^- and O_{2i}^{++} are separated in a large 144 atom supercell. We find that moving B_s^- away from O_{2i}^{++sq} by either one or two steps along the $\langle 110 \rangle$ chain of bonds results in an increase of energy of 0.38 eV in each case. Hence B_s^- is bound to O_{2i}^{++} by an energy of around 0.38 eV.

We note that the generation rate of the recombination centers is proportional to the initial concentration of O_{2i}^{++} in the crystal. In equilibrium, this is

$$[O_{2i}^{++}] \propto [O_{2i}] \exp\left(\frac{2[E(0/++) - E_F]}{kT}\right) \propto [B]^2, \quad (1)$$

where $E_F = kT \ln(N_v/[B])$ [31] has been used to determine the dependence upon boron concentration. Thus the generation rate is proportional to $[B]^2$ as observed [15]. Here N_v is the effective density of states of the valence band, $E(0/++)$ is the occupation level of the dimer with respect to the valence band E_v, E_F the Fermi level with respect to E_v and kT has its usual meaning.

The $B_sO_{2i}^{+}$ defect would anneal out in the dark, in the absence of excess minority carriers, with an activation energy, $E_A \sim E_B + E_m$ where E_B is the binding energy of O_{2i}^{++} to B_s^- and E_m is the migration energy of O_{2i}^{++}. Hence $E_A \sim 0.38 + 0.86 = 1.2$ eV in good agreement with an observed value of 1.3 eV. After capturing a minority carrier the complex will trap a majority carrier hole before it is able to dissociate. Therefore regardless of whether or not minority carriers are present, the defect will dissociate in the positive charge state with an activation energy $\sim$1.2 eV.

In summary, the calculations have shown that the B_sO_{2i} defect has a number of properties in common with the center responsible for the light-induced degradation of B-doped Cz-Si solar cells. It has a donor level close to that observed that acts as a carrier-recombination center and it anneals with the same activation energy $\sim$1.3 eV. Moreover, the dependence of its concentration on boron and oxygen is in agreement with observations. Its formation process is due to the trapping by boron of a O_{2i}^{++} species which diffuses rapidly with a barrier of only a few tenths of an eV under minority-carrier injection. These findings support the model for the center advanced by Schmidt *et al.*. We note that the presence of electrically active oxygen dimers is a crucial ingredient of the model. Evidence for the existence of an oxygen-related minority-carrier trap has long existed in *p*-Si [32,33]. The trap density increases with the oxygen concentration in both B-doped and Ga-doped material and its energy level has been placed around $E_c - 0.5$ eV and close to the $(+/++)$ level of O_{2i} found here [33].

Clearly it is desirable to reduce the concentration of dimers and/or the formation of the B-O_2 complex and several suggestions of how these can be done have been made previously. It is known that using Ga as the *p*-type dopant prevents degradation [8]. Preliminary calculations indicate that if B is replaced by Ga in the complex shown in Fig. 1, only the square form is stable. This complex has no deep levels and hence will not act as a carrier trap.

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