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A New Mechanism for Non-Radiative Recombination at Light-Induced Boron-Oxygen Complexes in Silicon

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ABSTRACT

First-principles study of BO_2 complex in B-doped Czochralski silicon (Cz-Si) reveals a novel, self-trapping-enhanced carrier recombination mechanism, in sharp contrasts to the standard fixed-level Shockley-Read-Hall theory for carrier recombination. We found that an O_2 dimer, distant from any B, would cause only weak carrier recombination under illumination — only enough to drive its diffusion to find B and form the BO_2 complexes. Surprisingly, BO_2 and O_2 produce nearly identical defect gap states. Despite this, recombination at BO_2 is substantially faster than that at O_2, because the charge state of the latter inhibits hole capture, the key step for such recombination.

1. Objectives

The improvement of solar cell performance is vital in the effort of reducing solar cell cost for market penetration, which is one of the most important goals in the Solar Program Multi-Year Technical Plan. It is known that the formation of the boron-oxygen-dimer (BO_2) complexes under light is the cause for the observed light-induced degradation (~1 % loss in absolute efficiency) in B-doped Cz-Si solar cells,[1, 2] which currently has about 25% of the market share for silicon. Our objective is to understand the degradation mechanism by studying atomic structures and electronic properties of the BO_2 complexes using first-principles calculations. Such understanding is vital in achieving better silicon materials for solar cell design with higher efficiencies.

2. Technical Approach

Our calculations are based on density functional theory within the local density approximation, as implemented in the VASP code.[3] The electron-ion interactions are described by ultra-soft pseudopotentials.[4] The valence wavefunctions are expanded in a plane-wave basis with a cutoff energy of 300 eV. Calculations were performed using both 64- and 216-atom supercells.

3. Results and Accomplishments

A previous study by Adey et al. had suggested that the BO_2-induced defect gap level causes the carrier recombination.[5] But this level (at 0.1 to 0.3 eV below the conduction band edge) is too shallow to act as an effective recombination center. Furthermore, our first-principles calculations showed a remarkable similarity between the defect levels introduced by BO_2 and O_2, as shown in Fig. 1.[6] Clearly, it is not a difference in the electronic gap levels that can explain why the BO_2 functions as a strong recombination center, but the uncomplexed O_2 does not.

Figures 2 (a) and (b) show the structures of the square (sq) and staggered (st) BO_2 complexes. For the uncomplexed O_2, the oxygen structures are basically the same as in Fig. 2. Figure 1(b) shows that the ground-state structure of the O_2 is square for the +2 charge state ($O_2^{sq,++}$) and staggered for the neutral charge state ($O_2^{st,0}$). We have calculated the binding energies of B with $O_2^{sq,++}$ and $O_2^{st,0}$ to be 0.55 and 0.41 eV, respectively.

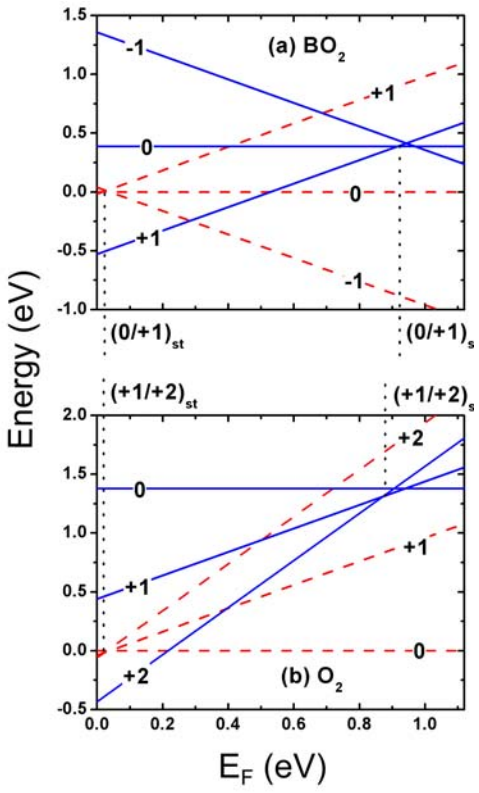

Fig. 1. Energies of (a) BO_2 and (b) uncomplexed O_2 in the square (solid lines) and staggered (dashed lines) configurations as functions of the Fermi level. The B binding sites in both square and staggered BO_2 complex are shown in Fig. 2(a) and (b) below. In this plot, we set the energies for the charge-neutral staggered configurations to zero. Dotted vertical lines indicate the primary recombination-active transition energies to emphasize the electronic similarities between the two different defects.

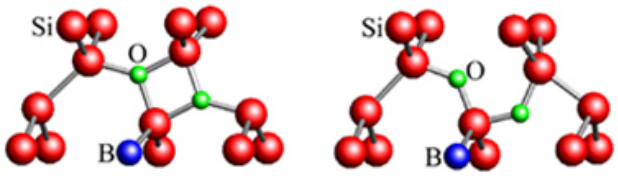

Fig. 2. (a) and (b) The most stable sq and st atomic structures for the BO_2 complexes.

In p-type Si, $BO_2^{sq,+}$ is the ground state of the BO_2 complex, with B^- bound to $O_2^{sq,++}$. In the dark, $BO_2^{sq,+}$ is separated from $BO_2^{st,+}$ by a high $sq \rightarrow st$ barrier of 0.82 eV. Under light, recombination takes place by carrier self-trapping, described by the four steps below:

$$(1)\ BO_2^{sq,+} + e^- \longrightarrow BO_2^{sq,0}$$
$$(2)\ BO_2^{sq,0} \xrightarrow{0.17\ eV} BO_2^{st,0}$$
$$(3)\ BO_2^{st,0} + h^+ \longrightarrow BO_2^{st,+}$$
$$(4)\ BO_2^{st,+} \xrightarrow{0.3\ eV} BO_2^{sq,+}\ .$$

Step (1) is the e^--trapping to a level at E_c – 0.2 eV where E_c is the conduction band minimum. The reconfiguration Step (2) is an e^- self-trapping process (over the 0.17-eV barrier), associated with a shallow-to-deep transition of the filled electron level. Step (3) is a fast h^+ trapping, which serves to reduce the $sq \rightarrow st$ barrier from 0.57 eV (for $BO_2^{st,0} \rightarrow BO_2^{sq,0}$) to 0.3 eV (for $BO_2^{st,+} \rightarrow BO_2^{sq,+}$), as indicated in the reconfiguration in Step (4). In somewhat a mirror of the Step (2), Step (4) reconfiguration is hole self-trapping process, associated with a shallow-to-deep transition of the hole-occupied level. These $sq \leftrightarrow st$ reconfigurations allow for the e^--h^+ pair energy (≈ bandgap energy) to be released through phonon vibrations. It is important to note that the recombination process described here is not mediated by a simple, fixed energy level. Instead, the defect level sweeps up and down within the bandgap in the process. This self-trapping enhanced recombination process requires a revision of the standard Shockley-Read-Hall analysis[7, 8] of carrier lifetimes,[9, 10] which is beyond the scope of the current paper. Although the BO_2 continually flips back and forth between the *sq* and *st* configurations induced by the carrier trapping, most of the BO_2 will either not dissociate or reform after dissociation, because of the 0.5-eV binding energy between B and O_2.

The $sq \leftrightarrow st$ reconfigurations of an uncomplexed O_2 have nearly identical barriers as the BO_2. In fact, as long as the B and O_2 share a common Si nearest neighbor, the B has little effect on the $sq \leftrightarrow st$ barriers. One may therefore naively assume that the same e^--h^+ recombination mechanism should also apply to the uncomplexed O_2. However, without the associated B, h^+-trapping to the positively charged O_2^+ must now overcome a repulsive capture barrier. It has been demonstrated that Coulomb repulsion normally decreases the capture probability by orders of magnitude.[11] This results in a slow recombination that is not expected to affect the minority carrier lifetime. Nevertheless, the repeated $sq \leftrightarrow st$ reconfigurations associated with the slow carrier recombination should be enough to drive the O_2 diffusion.

4. Conclusions

Our first-principles studies revealed a self-trapping-enhanced e^--h^+ recombination process for BO_2 in Czochralski Si. The new model explains that the change of the defect charge state drastically increases the recombination rate at the otherwise benign oxygen dimers, when they form metastable complexes with boron. Our results suggest new design principles to overcome photo-induced metastabilities either by excluding boron as the dopants, or by isolating boron from the diffusing uncomplexed O_2 dimers.

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