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 contrast 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, 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. The electron-ion interactions are described by ultra-soft pseudopotentials. 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. 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. 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$_{st,0}^{2+}$) and staggered for the neutral charge state (O$_{st,0}^{2+}$). We have calculated the binding energies of B with O$_{sq,0}^{2+}$ and O$_{st,0}^{2+}$ to be 0.55 and 0.41 eV, respectively.
In p-type Si, $\text{BO}_2^{4+}$ is the ground state of the $\text{BO}_2$ complex, with $\text{B}^-$ bound to $\text{O}_2^{2+}$. In the dark, $\text{BO}_2^{4+}$ is separated from $\text{BO}_2^{2+}$ by a high $\text{sq} \rightarrow \text{st}$ barrier of 0.82 eV. Under light, recombination takes place by carrier self-trapping, described by the four steps below:

1. $\text{BO}_2^{2+} + e^- \rightarrow \text{BO}_2^{3+}$
2. $\text{BO}_2^{3+} \rightarrow \text{BO}_2^{4+}$ (0.17 eV)
3. $\text{BO}_2^{4+} + h^+ \rightarrow \text{BO}_2^{5+}$
4. $\text{BO}_2^{5+} \rightarrow \text{BO}_2^{4+}$ (0.3 eV)

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 $\text{sq} \rightarrow \text{st}$ barrier from 0.57 eV (for $\text{BO}_2^{5+} \rightarrow \text{BO}_2^{5+}$) to 0.3 eV (for $\text{BO}_2^{5+} \rightarrow \text{BO}_2^{4+}$), 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 $\text{sq} \rightarrow \text{st}$ reconfigurations allow for the $e^- - h^+$ pair energy ($\approx$ 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 $\text{BO}_2$ continually flips back and forth between the sq and st configurations induced by the carrier trapping, most of the $\text{BO}_2$ will either not dissociate or reform after dissociation, because of the 0.5-eV binding energy between $\text{B}$ and $\text{O}_2$.

The $\text{sq} \rightarrow \text{st}$ reconfigurations of an uncomplexed $\text{O}_2$ have nearly identical barriers as the $\text{BO}_2$. In fact, as long as the $\text{B}$ and $\text{O}_2$ share a common Si nearest neighbor, the $\text{B}$ has little effect on the $\text{sq} \rightarrow \text{st}$ barriers. One may therefore naively assume that the same $e^- - h^+$ recombination mechanism should also apply to the uncomplexed $\text{O}_2$. However, without the associated $\text{B}$, $h^+$-trapping to the positively charged $\text{O}_2^+$ 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 $\text{sq} \rightarrow \text{st}$ reconfigurations associated with the slow carrier recombination should be enough to drive the $\text{O}_2$ diffusion.

4. Conclusions

Our first-principles studies revealed a self-trapping-enhanced $e^- - h^+$ recombination process for $\text{BO}_2$ 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 $\text{O}_2$ dimers.

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6. Formation energies were calculated according to S. B. Zhang, J. Phys.: Condens. Matter 14, R881 (2002).

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