First Principles Study of Boron in Amorphous Silicon

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ABSTRACT

We have carried out an ab initio simulation study of boron in amorphous silicon. In order to understand the possible structural environments of B atoms, we have studied substitutional-like (replacing one Si atom in the amorphous cell by a B atom) and interstitial-like (adding a B atom into an interstitial space) initial configurations. We have evaluated the Fermi-level dependent formation energy of the neutral and charged (±1) configurations and the chemical potential for the neutral ones. For the interstitial-like boron atom, we have find an averaged formation energy of 1.5 eV. For the substitutional case, we have found a dependence of the chemical potential on the distance to Si neighbors, which does not appear for the interstitial ones. From MD simulations, we could observe a diffusion event for an interstitial-like boron atom with a migration barrier of 0.6 eV.

INTRODUCTION

Future CMOS technology requires ultrashallow junctions with high dopant activation levels and very sharp doping profiles [1]. According to the ITRS [1], solid-phase epitaxial regrowth (SPER) of doped amorphous silicon (a-Si) is a promising technique to minimize channeling [2], transient-enhanced diffusion [3,4] and dopant deactivation [5,6] and it allows in the case of B to obtain high active concentrations of \(2-4\times10^{20}\) cm\(^{-3}\) [7,8], compared to \(2-9\times10^{19}\) cm\(^{-3}\) in c-Si [9,10]. Thus, for the fabrication of state-of-the-art electronic devices, preamorphization implants and high dopant implantation fluences are being used. Because of these reasons, there is an increasing interest in studying and modeling dopant processes in a-Si. B has been extensively studied in c-Si and diffusion mechanism [11-14], interaction with Si atoms and segregation processes [15-18] are well known. However, its behavior in a-Si has been studied to a much lesser degree, especially at the atomic level, apart from one early study [19].

The aim of this work is to understand the possible structural environments of B in a-Si and eventually its diffusion. Evidently, there will be a continuous range of configurations, unlike the discrete set obtained in a crystalline environment. The key dynamical features of B in a-Si are naturally formulated as hopping between various metastable configurations in the energy landscape, where of course the a-Si network has a high probability of rearranging and thus changing the energy landscape during annealing. Thus, we believe that this paper is an important step to the larger problem of unraveling the dynamics of B in a-Si.

SIMULATION DETAILS

We have carried out an ab initio study of B in a 64-atom a-Si cell. The most realistic computer models of a-Si are made using the algorithm of Wooten, Weaire and Winer (WWW) [20]. The WWW models are formed using a particular bond-switching algorithm, and extremely simple potentials. The cell used in this work was provided by D. A. Drabold using a model pro-
posed by Barkema and Mousseau (BM) [21], who developed an algorithm significantly improved from the original WWW scheme. The BM scheme guaranteed that there was no ‘crystal-line remnant’ in the WWW. Upon relaxing with \textit{ab initio} interactions, the BM model barely changes at all. To represent the amorphous environment faithfully, it is necessary to work with cells of at least several hundred atoms, and it is desirable to have even more. The difficulty with smaller models is that there are discernible strain effects (most notably in a slightly bloated bond angle distribution relative to experiment). Nevertheless, for local structural properties as we are focused on here, we anticipate that the strain artifacts are small. The cell properly includes the correct local topological disorder of the material, and it is big enough for a high-precision calculation that includes B.

For our \textit{ab initio} calculations, we have used the efficient density-functional theory code VASP [22]. We have performed our calculations with generalized gradient approximation (GGA) ultrasoft pseudopotentials [23], using a Monkhorst-Pack \textbf{k}-point sampling, 4\times4\times4 for the density of states calculation and 2\times2\times2 for the ionic relaxations. The energy cutoff chosen was 230 eV. For the substitutional-like B atoms (B\textsubscript{s}), we replaced one of the Si atoms by B. For the interstitial-like ones (B\textsubscript{i}), we either placed a B atom in an interstitial site or added an interstitial Si atom next to a B\textsubscript{s}. Subsequently, we carried out a relaxation of both the atomic positions and cell shape and volume. For our \textit{ab-initio} MD simulations, we used an energy cutoff of 156 eV and \textit{Γ}-point sampling.

\textbf{RESULTS AND DISCUSSION}

Since we wanted to include charge effects into our study, we first calculated the electronic density of states (DOS) in the amorphous cell to evaluate its band gap. In the case of c-Si, \textit{ab initio} calculations give an incorrected value of 0.63 eV for the gap [24] instead of the experimental value of 1.12 eV (at 300 K). However, \textit{ab initio} calculations can be corrected with scissor, finite-size, and gap-state corrections [24]. For a-Si, the \textit{ab initio} calculation finds a gap of 0.76 eV, 21\% larger than c-Si. As a first approximation, we can estimate the corrected gap value to be 21\% larger than the experimental value for c-Si. This gives a gap value of 1.36 eV for a-Si, which is in agreement with experiments, where it ranges from 1.2 to 1.6 eV [25, 26].

For charged B atoms in the amorphous cell, the formation energy (\(E_f\)) for a system with charge \(Q\) as a function of the Fermi level (\(E_F\)) can be calculated from the expression

\[
E_f = E_{\text{tot}}(Q) - E_{\text{ref}} + Q(E_v + E_F),
\]

where \(E_{\text{tot}}(Q)\) is the total energy of the charged system, \(E_{\text{ref}}\) is a neutral reference energy (\(E_{\text{ref}} = E_{\text{tot}}(aSi_{63}B) + E_{\text{tot}}(aSi_{64})/64\) for B\textsubscript{i} in a 64-atom supercell), and \(E_v\) is the energy of the top of the valence band. In order to evaluate the variation of energy when adding/removing one electron, we have only considered those cells in which there were not any coordination changes during this process. Then, for the different coordinations of B atoms (fourfold for B\textsubscript{s} and three, four and fivefold for B\textsubscript{i}), we have evaluated the Boltzmann averaged formation energy at 650°C,

\[
\langle E_f \rangle = \frac{\sum E_f e^{-E_f/\hbar \omega T}}{\sum e^{-E_f/\hbar \omega T}}.
\]
In Fig. 1 we plot the formation energy of B atoms relative to $B_s^0$ as a function of the Fermi level. Figure 1(a) shows that $B_s^-$ has a lower energy than both $B_s^0$ and $B_s^+$ for the entire Fermi-level range. Therefore, $B_s$ will be negatively charged for all Fermi level values. In the case of $B_i$, both +1 and −1 charge states can be stable (with a very small stability range for neutral $B_i(3)$). The difference in formation energy between $B_s$ and $B_i(4)$ is small. They also have a similar energy dependence on the Fermi level. This suggests that $B_i(4)$ and $B_s$ are similar (substitutional, but with changed a-Si network). The midgap energies correspond in all cases to the negative charge state. Taking the lowest-energy configuration, $B_s^-$, as reference, they are $E(B_s^- (4)) = 0.30$ eV, $E(B_i^- (3)) = 1.53$ eV, and $E(B_i^- (5)) = 1.55$ eV. Since $B_i(4)$ can be considered as a substitutional-like configuration and $B_i(3)$ and $B_i(5)$ have nearly identical Boltzmann-averaged formation energies, there seems to be a well defined formation energy for interstitial-like B of $\sim 1.54$ eV at midgap.

The chemical potential of B atoms, $\mu_B$, can be calculated as

$$\mu_B = E_{tot}(a\text{-}Si_nB) - n E_{tot}(a\text{-}Si_{64})/64$$

where $n$ indicates the number of Si atoms in the cell, 63 for $B_s$ and 64 for $B_i$ (in our case, $E_{tot}(a\text{-}Si_{64})/64 = -5.25$ eV defines the Si chemical potential). Figure 2 shows the B chemical potential as a function of the average bond length between the B atom and its nearest neighbors. 62.5\% of $B_s$ configurations are inside the limits marked by the straight dashed lines. Solid line corresponds to a linear fitting of these configurations. Figure 2 shows that there is more scattering in the data for $B_i$ than for the $B_s$ data. Chemical potential values scatter within an interval of $\sim 1.4$ eV for $B_s$ and $\sim 3$ eV for $B_i$. This wide distribution of values makes the identification of any particularity in the local structures of B atoms in $a$-Si tedious. However, it can be seen in Fig. 2 that the $B_s$ configurations within the dashed lines represent a linear trend: the closer the
neighbors, the lower the chemical potential. This indicates that there seems to be a dependence of the chemical potential on the local environment of B
s
atoms. This linear trend appears to be a lower limit to almost all B
i
configurations. Figure 2 also shows that B
i
(4) configurations do not display the same trends as B
s
and show considerably more scattering. Although the Boltzmann averaged formation energy is higher for B
i
than for B
s
, the lowest chemical potential corresponds to a (substitutional-like) B
i
(4) configuration.

**Figure 2.** Chemical potential of B
i
and B
s
as a function of their average bond length to nearest Si neighbor atoms for the different coordinations considered. 62.5% of B
s
configurations are inside the limits marked by the dashed lines. Solid line corresponds to a linear fitting of these points.

In order to analyze the dynamical features of B in a-Si, we have used several B
i
and B
s
configurations as the starting point of *ab initio* molecular dynamics (MD) simulations at 1000 K. We found that within the simulated time (around 55 ps) none of the MD simulations of B
s
configurations showed any migration of the B atom. However, local rearrangements (bond switching) of Si-Si bonds have been observed in the cell. On the other hand, we observed a diffusion event in one of the B
i
(3) configuration. This diffusion event was analyzed using the Nudged-elastic Band Method (NEBM) [27] implemented into VASP in order to obtain the energy barriers along the path. We used configurations obtained with MD as initial, intermediate and final points. Figure 3 shows the nudged-elastic band total energy along the diffusion path together with some snapshots of the B environment at the marked points. The highest forward barrier, which represents the overall migration energy from initial to final configuration, is ~0.6 eV (similar to the value for crystalline Si [14]). Intermediate forward barriers range from ~0.3 to ~0.6 eV and may indicate a possible range for migration barriers. The highest reverse barrier measures ~ 0.9 eV. It can be seen from the snapshots that in some cases the barriers correspond to Si rearrangement. These rearrangements of the amorphous structure at high temperatures could drag B atoms along (or not). Thus, they cannot really be separated from the more traditional B migration (mostly unchanged cell), which makes further studies difficult. However, further studies on diffusion are required to have a statistic result for the migration energy.
CONCLUSIONS

We have carried out an ab initio study of B in a-Si. From the calculation of the DOS in the amorphous reference cell we obtained a band gap higher that in the crystalline case, in agreement with experiments. For B atoms in a-Si, we have started considering initially substitutional-like and interstitial-like configurations. In the analysis of the dependence of their formation energy as a function of the Fermi level, we have found that B$_s$ behaves similarly to the crystalline case. In the case of B$_i$, it is positively charged for highly p-doped a-Si for all coordinations and will change to the negative state with increasing value of the Fermi level. At midgap, B$_i$ has a formation energy of ~1.5 eV. From the analysis of the chemical potential, we found that most of the B$_s$ configurations display a linear trend: the closer the Si neighbors, the lower the chemical potential. This trend can be used as a first step to identify any local structure of B atoms in a-Si.

MD simulations showed that Si bond switching can influence the diffusion processes when increasing the temperature. Any further study of diffusion in a-Si will have to separate the influence of the changes in the network from the diffusion processes of B atoms. As a first attempt, we have obtained from our NEBM simulations the order of magnitude for energy barriers (~0.6 eV).

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