Prediction of \( B-\text{Si}_\text{i}-\text{F} \) complex formation and its role in \( B \) transient enhanced diffusion suppression and deactivation

Scott A. Harrison, Thomas F. Edgar, and Gyeong S. Hwang

Department of Chemical Engineering, University of Texas, Austin, Texas 78713

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Gradient corrected density functional calculations are used to examine the interaction of boron and fluorine in crystalline silicon. We have determined the formation of a stable boron-silicon-fluorine (\( B-\text{Si}_\text{i}-\text{F} \)) complex in which the \( B \) and \( \text{F} \) atoms are indirectly connected through a Si interstitial, while the direct \( B-\text{F} \) bonding interaction is likely to be insignificant. Depending on dissociation reactions, the binding energy of the \( B-\text{Si}_\text{i}-\text{F} \) complex is predicted to be \( 1.82-1.91 \) eV relative to the corresponding products in the neutral state. We also show the atomic structure and bonding mechanism of \( B-\text{Si}_\text{i}-\text{F} \) and discuss the potential role of \( B-\text{Si}_\text{i}-\text{F} \) formation in \( B \) transient enhanced diffusion suppression and deactivation. © 2007 American Institute of Physics.

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An early experimental study\(^1\) showed that \( B \) implanted into \( \text{F} \) preamorphized silicon resulted in shallower junctions and better activation than a molecular \( \text{BF}_2 \) implant. A subsequent study\(^2\) showed that the benefits from \( \text{F} \) coimplantation can be attributed to a chemical effect that is independent of the benefits due to preamorphization. A series of recent experimental\(^3\)–\(^6\) and theoretical\(^7\) studies have suggested that the benefits of the \( \text{F} \) coimplant would be due to the formation of \( \text{F} \)-vacancy complexes that act as traps to suppress the transient enhanced diffusion suppression and deactivation. While there is no significant direct-bonding interaction between \( B \) and \( \text{F} \), our calculations predict that \( B \) and \( \text{F} \) atoms can strongly interact through a Si atom. Based on the results, we discuss the possible role of \( B-\text{Si}_\text{i}-\text{F} \) formation in \( B \) transient enhanced diffusion suppression and deactivation during postimplantation annealing.

Using the well-established Vienna \textit{ab initio} simulation package (VASP),\(^12\) all atomic structures and energies reported herein were calculated within the generalized gradient approximation\(^13\) (PW91) to density functional theory (DFT). A plane-wave basis set for valence electron states and Vanderbilt ultrasoft pseudopotentials\(^14\) for core-electron interactions were employed. We used a plane-wave cutoff energy of 320 eV and a \((2 \times 2 \times 2)\) Monkhorst-Pack mesh of \( k \) points\(^15\) to sample the Brillouin zone. All defect systems examined were modeled using 216-atom supercell with a fixed lattice constant of 5.457 Å. All atoms were fully relaxed using the conjugate gradient method until residual forces on constituent atoms become smaller than \( 5 \times 10^{-2} \) eV/Å.

The charging of impurity/dopant was carefully assessed by computing defect ionization levels \((\mu_v)\). At a given Fermi level \((\epsilon_F)\), the relative formation energy of a charged defect in charge state \( q = \pm 1 \) to a neutral defect is given by \( E_v^q - E_v^0 = q(\epsilon_F - \mu_v) \), where \( \epsilon_F \) is given relative to the valence band maximum \((E_v)\). Thus, the defect levels can be approximated by \( E_v + q(E_v^0 + \mu_v) = E_v^0 \), where \( E_v^0 \) and \( E_v^q \) are the total energies of the defects in \( q \) and neutral charge states, respectively, and \( E_v^0 \) is the position of the valence band maximum in supercell \( E_v^0 \). In calculating a charged defect, a homogeneous background charge is included to maintain the overall charge neutrality in the periodic supercell. To account for the Coulomb energy between the charged defect and the background charge, a monopole correction is made to the total energy of the charged system.\(^16\) Assuming a pointlike +1 charge defect in the 216-atom supercell, the monopole correction is estimated to be approximately 0.12 eV.

\textbf{Structure and stability.} Figure 1 shows the predicted ground-state structure of the neutral \( B-\text{Si}_\text{i}-\text{F} \) complex in which the \( B \) and \( \text{Si} \) atoms are aligned in the [100] direction while sharing a lattice site, and the \( \text{F} \) atom is bonded to the
Si atom. In this configuration, the B atom exhibits distorted $sp^2$ hybridization, whereas the Si atom is likely to have more $sp^3$-like character given the significant departure from the ideal $sp^2$ planar bonding configuration. In addition, the nature of Si–F bond appears to be polar covalent with some charge transfer from Si to F. The bonding configuration suggests that the $B_i$–Si$_i$–F$_i$ complex is electrically inactive and very unlikely to undergo diffusion.

To examine the thermal stability of the $B_i$–Si$_i$–F$_i$ complex, we calculated its binding energies relative to products associated with potential dissociation reactions. In addition to F and Si$_i$ atoms, recent theoretical studies have identified that $B_i$–Si$_i$ and F$_i$–Si$_i$ pairs are also mobile. Hence, we expect that $B_i$–Si$_i$–F$_i$ dissociation may take place yielding the following sets of products: (i) $B_i$–Si$_i$+$F_i$, (ii) $B_i$+$F_i$–Si$_i$, or (iii) $B_i$–F$_i$+Si$_i$. For each reaction the $B_i$–Si$_i$–F$_i$ binding energy can be given as the sum of the formation energies of corresponding dissociation products less the $B_i$–Si$_i$–F$_i$ formation energy.

Figure 2 shows the relative formation energies of the potential dissociation products such as $B_i$–Si$_i$, F, F$_i$–Si$_i$, and Si$_i$ at different charge states and configurations with the Fermi level for the computed Si gap of 0.63 eV, with respect to neutral $B_i$ ($B_i^0$) and bond-centered F ($F_{bc}$). Here, the formation energies of neutral Si$_i$, $B_i$–Si$_i$, and F$_i$–Si$_i$ defects are calculated by $E_i[Si]_i$=[$E[Si]$–1217/216$E[Si]_{216}$], $E_i[B]_{216}$=[$E[BSi]_{216}$]–[$E[BSi]_{216}$]–$E[Si]_{216}$/216, and $E_i[F]_{216}$=[$E[BSi]_{216}$]–[$E[BFSi]_{216}$]–[$E[FSi]_{216}$], where $E[BSi]_{216}$, $E[BSi]_{216}$, $E[BSi]_{216}$, $E[FSi]_{216}$, and $E[Si]_{216}$ are the total energies of the 216-atom supercells with $B_i$–Si$_i$, $B_i^0$, $B_i$–F$_i$, and no defect, respectively. The relative formation energies of charged defects are given based on their predicted ionization levels. The first donor and/or acceptor levels of $B_i$–Si$_i$, F, F$_i$–Si$_i$, and Si$_i$ are in good agreement with previous theoretical results. For the same reference state of $B_i^0$ and $F_{bc}$, the $B_i$–F$_i$ and $B_i$–Si$_i$–F$_i$ formation energies are estimated to be –1.10 and 0.78 eV, respectively. Note that the values of the relative formation energies are dependent on the chosen reference states, while the binding energies are not. For instance, if the $B_i$ ground state ($B_i^0$) is taken as reference, under intrinsic conditions the relative defect formation energies will overall increase by 0.51 eV at room temperature, given the actual Si band gap of 1.12 eV and the first B acceptor level (–/0) of 0.05 eV.

Based on the predicted relative formation energies, we evaluated the binding strength of $B_i$–Si$_i$–F$_i$ for each disso-
cation reaction. Firstly, for the $\text{B}_i-\text{Si}_i-\text{F}_i \rightarrow \text{B}_i-\text{Si}_i+\text{F}$ reaction, at the computed midgap the $\text{B}_i-\text{Si}_i-\text{F}_i$ binding energy is predicted to be 1.91 eV relative to the neutral dissociation products $\text{F}_i^0$ and $\text{B}_i-\text{Si}_i^0$ and is expected to get lower to 1.40 eV upon dissociation into more stable ionized products such as $\text{B}_i-\text{Si}_i^+$ and $\text{F}_i^+$ (see Fig. 2). Considering the lower formation energies of the positive products, the $\text{B}_i-\text{Si}_i-\text{F}_i$ complex may dissociate more easily in a heavily B-doped (extrinsic) region. Secondly, for the $\text{B}_i-\text{Si}_i-\text{F}_i \rightarrow \text{B}_i+\text{Si}_i-\text{F}_i$ reaction, under intrinsic conditions the $\text{B}_i-\text{Si}_i-\text{F}_i$ binding energy is estimated to be 1.84 eV relative to the neutral dissociation products $\text{B}_i^0$ and $\text{Si}_i^0$ and approximately 1.33 eV (≈1.84−0.51) relative to more stable products $\text{B}_i$ and $\text{Si}_i$ in intrinsic regions at room temperature. Finally, the binding energy of $\text{B}_i-\text{Si}_i-\text{F}_i$ relative to the neutral dissociation products $\text{F}_i\text{bc}-\text{B}_i$ and $\text{Si}_i^0$, i.e., $\text{B}_i-\text{Si}_i-\text{F}_i \rightarrow \text{B}_i-\text{Si}_i^0$ is calculated to be 1.82 eV. The sizeable binding energies of 1.82−1.91 eV from the neutral-state calculations clearly suggest the formation of a stable $\text{B}_i-\text{Si}_i-\text{F}_i$ complex in Si, although precise determination of $\text{B}_i-\text{Si}_i-\text{F}_i$ thermal stability may require further calculations of the dissociation pathways and corresponding activation energies. On the other hand, the binding energy of $\text{B}_i-\text{F}_i$ is predicted to be 1.10 eV relative to the neutral dissociation products $\text{B}_i^0$ and $\text{F}_i^0$ and reduces to 0.59 eV (≈1.10−0.51) with respect to $\text{B}_i$ in intrinsic regions at room temperature. The $\text{B}_i-\text{F}_i$ binding strength can be expected to substantially decrease further considering the more stable positive product $\text{F}_i^+$ [see Fig. 2(b)], i.e., $\text{B}_i-\text{F}_i \rightarrow \text{B}_i^++\text{F}_i^+$. The predicted weak binding of $\text{B}_i-\text{F}_i$ can support recent experimental results that show no significant direct interaction between $\text{B}$ and $\text{F}$.4,10

**Implications.** Next we discuss the potential influence of $\text{B}_i-\text{Si}_i-\text{F}_i$ formation on the TED suppression and deactivation of implanted B during postimplantation annealing. As mentioned earlier, recent experiments conducted by Cowern et al.6 have demonstrated that B TED suppression and deactivation occur when $\text{F}$ and $\text{B}$ profiles overlap, whereas both B TED suppression and high B activation can be achieved if the $\text{F}$ profile is implanted deeper than the $\text{B}$ profile. In the case of the overlapping $\text{B}$ and $\text{F}$ profiles, we can expect that the high-concentration $\text{B}$ and $\text{F}$ atoms will react with Si interstitials (released from end-of-range defects) to form $\text{B}_i-\text{Si}_i-\text{F}_i$ complexes (and/or $\text{B}_i-\text{Si}_i-\text{F}_i$ associated larger clusters), thereby leading to B TED suppression and B deactivation. Since $\text{B}_i-\text{Si}_i-\text{F}_i$ formation is dependent on the local concentrations of $\text{B}$, $\text{F}$, and $\text{Si}$, we expect that the influence of $\text{B}_i-\text{Si}_i-\text{F}_i$ complexes would become minimal if any of the $\text{B}$, $\text{Si}$, and $\text{F}$ concentrations are insufficient at a given annealing temperature. The strong concentration-dependent behavior may help explain why some experimental results show the insignificant interaction between $\text{B}$ and $\text{F}$ even though $\text{B}$ and $\text{F}$ profiles overlap.4,10 The existence of $\text{B}_i-\text{Si}_i-\text{F}_i$ complexes also lends support to the idea that the F coimplant can prevent B TED in more than one way, particularly in a region where both $\text{B}$ and $\text{F}$ concentrations are sufficiently high. That is, the $\text{B}_i-\text{Si}_i-\text{F}_i$ complex may directly impede the diffusion of $\text{B}_i-\text{Si}_i$ pairs, while F-vacancy traps may suppress the Si concentration and thus reduces the likelihood of mobile $\text{B}_i-\text{Si}_i$ pair formation.

In summary, we have identified the structure of neutral $\text{B}_i-\text{Si}_i-\text{F}_i$ in which the $\text{B}$ and $\text{Si}$ atoms are aligned in the [100] direction while sharing a lattice site, and the $\text{F}$ atom is bonded to the $\text{Si}$ atom. The structural analysis suggests that the $\text{B}_i-\text{Si}_i-\text{F}_i$ complex is electrically inactive and very unlikely to undergo diffusion. While no significant direct $\text{B}-\text{F}$ bonding interaction is expected,4,10 the formation of $\text{B}_i-\text{Si}_i-\text{F}_i$ (and/or its associated larger clusters) can be considered a possible origin of $\text{B}-\text{F}$ interaction responsible for B deactivation in a region where both $\text{B}$, $\text{F}$, and $\text{Si}$ concentrations are sufficiently high, as shown by recent experiments.6 Our results also suggest that the F coimplant could prevent B TED in more than one way, depending on the local concentrations of $\text{B}$, $\text{F}$, and $\text{Si}$; that is, the $\text{B}_i-\text{Si}_i-\text{F}_i$ complex may directly impede the diffusion of $\text{B}_i-\text{Si}_i$ pairs, while F-vacancy traps may suppress the Si concentration and thus reduces the likelihood of mobile $\text{B}_i-\text{Si}_i$ pair formation. The fundamental findings will assist in developing a better understanding of the anomalous behavior of coimplanted F atoms as well as an improved physical model, which can contribute to optimizing the use of F as a coimplant in ultrashallow junction formation.

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