

Prediction of B–Si_i–F complex formation and its role in B transient enhanced diffusion suppression and deactivation

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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_s–Si_i–F_i) complex in which the B and F atoms are indirectly connected through a Si interstitial, while the direct B–F bonding interaction is likely to be insignificant. Depending on dissociation reactions, the binding energy of the B_s–Si_i–F_i 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_s–Si_i–F_i and discuss the potential role of B_s–Si_i–F_i formation in B transient enhanced diffusion suppression and deactivation. © 2007 American Institute of Physics.

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An early experimental study¹ showed that B implanted into F preamorphized silicon resulted in shallower junctions and better activation than a molecular BF₂ implant. A subsequent study² showed that the benefits from 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^{5,7} studies have suggested that the benefits of the F coimplant would be due to the formation of F-vacancy complexes that act as traps to suppress the population of Si interstitials, which are known to mediate B transient enhanced diffusion (TED) and clustering. Indeed, previous positron annihilation spectroscopy measurements have identified the presence of F-vacancy complexes.^{8,9} While F-vacancy complexes seem to play a key role in providing the benefits of F coimplantation, experimental results have also suggested that F can interact with interstitial Si (Refs. 9 and 10) as well as with B,^{6,11} although the B–F interaction remains a source of controversy. While one group of researchers¹¹ has claimed that the direct interaction between B and F could suppress B TED, the other group^{4,10} has suggested that there would be no significant direct B–F interaction. Very recently Cowern *et al.*⁶ reported that overlapping B and F profiles can result in B TED suppression at the cost of B deactivation, while both B TED suppression and high B activation can be achieved if the F profile is implanted deeper than the B profile. Based on the observations, they advocated that the F–B interaction results in B deactivation while interstitials are suppressed by F-vacancy traps. However, the origin of the F–B interaction is ambiguous.

In this paper, we present the structure, stability, and bonding mechanism of a B_s–Si_i–F_i complex based on density functional calculations. Here the subscripts *s* and *i* indicate substitutional and interstitial, respectively. The thermal stability of the B_s–Si_i–F_i complex is examined by calculating its binding energies relative to products associated with potential dissociation reactions. While there is no significant

direct-bonding interaction between B and F, our calculations predict that B and F atoms can strongly interact through a Si atom. Based on the results, we discuss the possible role of B_s–Si_i–F_i formation in B TED suppression and deactivation during postimplantation annealing.

Using the well-established Vienna *ab initio* simulation package (VASP),¹² all atomic structures and energies reported herein were calculated within the generalized gradient approximation¹³ (PW91) to density functional theory (DFT). A plane-wave basis set for valence electron states and Vanderbilt ultrasoft pseudopotentials¹⁴ for core-electron interactions were employed. We used a plane-wave cutoff energy of 320 eV and a (2 × 2 × 2) Monkhorst-Pack mesh of *k* points¹⁵ 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 × 10^{–2} eV/Å.

The charging of impurity/dopant was carefully assessed by computing defect ionization levels (μ_i). At a given Fermi level (ε_F), the relative formation energy of a charged defect in charge state *q* = ±1 to a neutral defect is given by $E_f^q - E_f^0 = q(\epsilon_F - \mu_i)$, where ε_F is given relative to the valence band maximum (E_V). Thus, the defect levels can be approximated by $E_D^q + q(E_v^q + \mu_i) = E_D^0$, where E_D^q and E_D^0 are the total energies of the defects in *q* and neutral charge states, respectively, and E_v^q is the position of the valence band maximum in supercell E_D^q . 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.

Structure and stability. Figure 1 shows the predicted ground-state structure of the neutral B_s–Si_i–F_i complex in which the B and Si atoms are aligned in the [100] direction while sharing a lattice site, and the F atom is bonded to the

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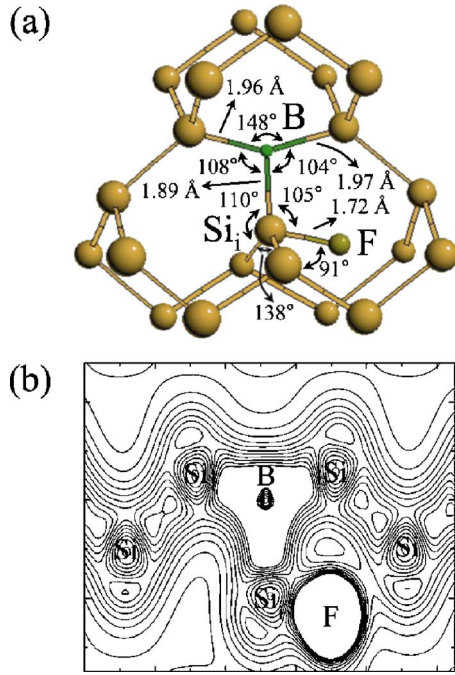


FIG. 1. (Color online) The (a) B-Si-F structure and (b) a contour plot of the valence charge density of the plane defined by B, Si, and F in the B-Si-F structure.

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_s -Si-F_i complex is electrically inactive and very unlikely to undergo diffusion.

To examine the thermal stability of the B_s -Si-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_s -Si_i and F_i-Si_i pairs are also mobile. Hence, we expect that B_s -Si-F_i dissociation may take place yielding the following sets of products: (i) B_s -Si_i+F_i, (ii) B_s +F_i-Si_i, or (iii) B_s -F_i+Si_i. For each reaction the B_s -Si-F_i binding energy can be given as the sum of the formation energies of corresponding dissociation products less the B_s -Si-F_i formation energy.

Figure 2 shows the relative formation energies of the potential dissociation products such as B_s -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_s (B_s^0) and bond-centered F (F_{bc}^0). Here, the formation energies of neutral Si_i, B_s -Si_i, and F_i-Si_i defects are calculated by $E_f(Si_i^0) = E[Si_{217}] - (217/216)E[Si_{216}]$, $E_f(B_s-Si_i^0) = E[B_{Si_{216}}] - E[B_{Si_{215}}] - E[Si_{216}]/216$, and $E_f(B_s-F_i) = E[BFSi_{215}] - E[B_{Si_{215}}] - E[FSi_{216}]$, where $E[B_{Si_{216}}]$, $E[B_{Si_{215}}]$, $E[BFSi_{215}]$, $E[FSi_{216}]$, and $E[Si_{216}]$ are the total energies of the 216-atom supercells with B_s -Si_i⁰, B_s^0 , B_s -F_i, F, 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

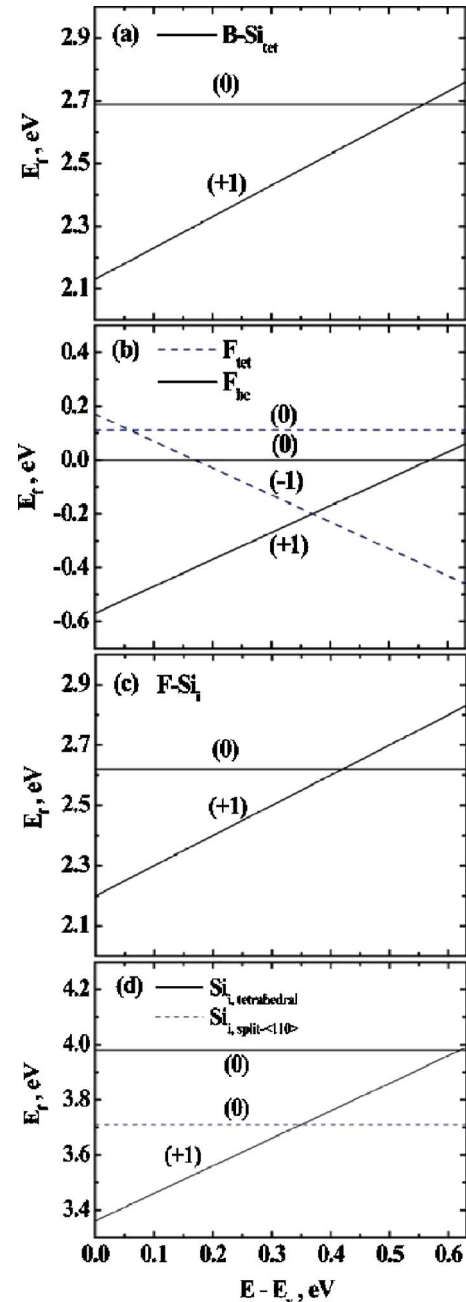


FIG. 2. (Color online) Relative formation energies (in eV) of (a) the B-Si pair, (b) the F interstitial, (c) the F-Si pair, and (d) the Si_i interstitial in different charge states as a function of the Fermi level. The reference states are B_s^0 and F_{bc}^0 . The plots are scaled in terms of the computed generalized gradient approximation (GGA) Si gap of 0.63 eV.

levels of B_s -Si_i, F, F_i-Si_i, and Si_i are in good agreement with previous theoretical results.^{5,7,17,18} For the same reference state of B_s^0 and F_{bc}^0 , the B_s -F_i and B_s -Si-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_s ground state (B_s^-) 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.¹⁹

Based on the predicted relative formation energies, we evaluated the binding strength of B_s -Si-F_i for each disso-

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

Implications. Next we discuss the potential influence of $B_s-Si_i-F_i$ 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 F and B profiles overlap, whereas both B TED suppression and high B activation can be achieved if the F profile is implanted deeper than the B profile. In the case of the overlapping B and F profiles, we can expect that the high-concentration B and F atoms will react with Si interstitials (released from end-of-range defects) to form $B_s-Si_i-F_i$ complexes (and/or $B_s-Si_i-F_i$ associated larger clusters), thereby leading to B TED suppression and B deactivation.

Since $B_s-Si_i-F_i$ formation is dependent on the local concentrations of B, F, and Si_i , we expect that the influence of B– Si_i –F complexes would become minimal if any of the B, Si_i , and 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 B and F even though B and F profile overlap.^{4,10} The existence of $B_s-Si_i-F_i$ 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 B and F concentrations are sufficiently high. That is, the $B_s-Si_i-F_i$ complex may directly impede the diffusion of B_s-Si_i pairs, while F-vacancy traps may suppress the Si_i

concentration and thus reduces the likelihood of mobile B– Si_i pair formation.

In summary, we have identified the structure of neutral $B_s-Si_i-F_i$ in which the B and Si atoms are aligned in the [100] direction while sharing a lattice site, and the F atom is bonded to the Si atom. The structural analysis suggests that the $B_s-Si_i-F_i$ complex is electrically inactive and very unlikely to undergo diffusion. While no significant direct B–F bonding interaction is expected,^{4,10} the formation of $B_s-Si_i-F_i$ (and/or its associated larger clusters) can be considered as a possible origin of B–F interaction responsible for B deactivation in a region where both B, F, and Si_i 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 B, F, and Si_i ; that is, the $B_s-Si_i-F_i$ complex may directly impede the diffusion of B_s-Si_i pairs, while F-vacancy traps may suppress the Si_i concentration and thus reduces the likelihood of mobile B– 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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