

***Ab initio* modeling and experimental study of C–B interactions in Si**

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We present results of *ab initio* calculations for the structure and energetics of small boron-carbon-interstitial and carbon-interstitial clusters in silicon and a respective continuum model for the nucleation, growth, and dissolution of these clusters. To test our calculations, we also measure secondary-ion mass spectra of boron and carbon in a SiGeCB system, which our model reproduces well. For the considered concentration regime, we find rapid carbon diffusion, nearly immobile boron, and undersaturation of silicon self-interstitials, resulting mainly from two clusters suggested by our *ab initio* results, the dicarbon-interstitial cluster and the boron-carbon-interstitial cluster. © 2002 American Institute of Physics. [DOI: 10.1063/1.1430505]

SiGeC has several advantageous materials properties compared to SiGe, which include the compensation of film strains by the adjustment of the Ge/C ratio, enhanced thermal stability, increased critical film thickness, suppressed transient enhanced diffusion (TED) of boron, and preservation of the narrowed band gap of strained SiGe. One particular device application of SiGeC films is the construction of heterojunction bipolar transistors (HBTs) using Si/SiGeC/Si heterostructures. SiGeC HBTs have improved performance (higher frequency) due to the smaller band gap¹ and stability of the base profile. Whereas the changes in diffusion due to the addition of Ge to Si can be captured by a simple extension,² the addition of C poses more fundamental challenges and thus requires a more fundamental investigation.

The currently prevalent explanation of the suppression of diffusion of boron by carbon is that carbon reduces the free silicon interstitial (*I*) concentration by forming a to date unspecified C–*I* complex, resulting in fewer B–*I* pairs, which are believed to be responsible for B, TED in Si.³ It further shows that the diffusion of carbon incorporated into silicon well above its solid solubility causes an undersaturation of silicon self-interstitials, which further retards boron diffusion.

In this work, we explore the atomic mechanisms for the effect of carbon on B diffusion in more depth through *ab initio* investigation of C–C and C–B interactions. In this work, we used the Vienna *ab initio* simulation package (VASP)⁴ within the generalized-gradient approximation (GGA) for the first-principles calculations. A supercell of 64 Si atoms and a cutoff energy of 21 Ry were chosen for all calculations. Diffusion barriers were determined using the nudged elastic band method⁵ implemented in VASP, which determines a (local) minimum energy diffusion path once the initial and final geometries are chosen. We have used this method in the past, e.g., to determine dopant diffusion at Pt grain boundaries,⁶ the B diffusion mechanism,⁷ or C incorporation mechanisms by surface diffusion processes,⁸ and have found it to be reliable and efficient. Total energies for

charged states were calculated similarly to Ref. 7. All energies are reported for the midgap position of the Fermi level.

We calculated the total energies of substitutional carbon in Si at different charge states. As expected, neutral substitutional carbon is the most stable charge state at midgap. In comparison, the most stable charge state for B in Si is -1 .⁷

We find for CI pairs in the previously discussed⁹ $\langle 100 \rangle$ split configuration the neutral charge state to have the lowest energy, 0.19 (0.56) eV lower than the -1 ($+1$) state at midgap. We calculate the binding energies for a neutral CI split interstitial to be 1.75 eV, in good agreement with a value of 1.63 eV extracted from experimental values.¹⁰ There, we take the neutral Si interstitialcy (two Si atoms occupying a single Si lattice site in form of a $\langle 110 \rangle$ dumbbell) and a neutral substitutional carbon as references. In comparison, the theoretical binding energy for a BI split interstitial is 0.80 eV.⁷ Using the nudged elastic band method, we obtained a value of 0.56 eV for the CI migration energy, consistent with the value of 0.50 eV from previous work by Capaz *et al.*⁹ and comparable to the experimental values of 0.73–0.88 eV.^{10,11}

Extensive investigations from first principles have been performed in the past for B–B¹² and C–C interactions.^{9,13,14} For both elements, it has been found that substitutional pairs on neighboring sites have a repulsive interaction energy, ~ 0.9 eV in the case of B,¹³ and ~ 1.8 eV in the case of C.¹⁴ Therefore, we can safely exclude substitutional B–C pairs as the dominant configuration. Since both impurities are known to form pairs with self-interstitials rather than with vacancies and have an interstitial-assisted diffusion mechanism, we thus postulate that the dominant B–C pair must involve a Si self-interstitial. The lowest-energy structure for B₂I (Ref. 12; for this structure, extensive minimizations have been performed and many competing configurations have been examined) and C₂I pairs [Fig. 1(c)] have been found to be a $\langle 100 \rangle$ split dumbbell. Thus, we assumed that the same structure would have at least a competitively low energy for the mixed CBI pair [Fig. 1(d)]. The total energies of the C–B split interstitials in $\langle 100 \rangle$ and $\langle 111 \rangle$ orientation were calculated to be 0.55 eV and 1.59 eV higher than that of the $\langle 100 \rangle$ dumb-

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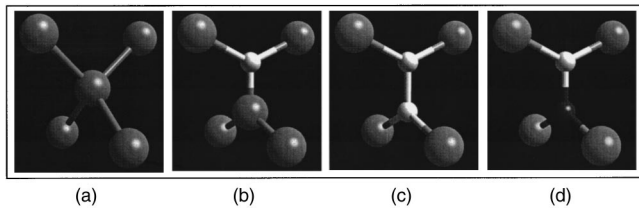


FIG. 1. The different defects in comparison to a perfect Si atom (a), which is displayed with its four nearest neighbors. Shown are the carbon-interstitial pair (b), the C_2I cluster (c), and the BCI cluster (d). Si atoms are represented by large gray balls, C (B) by bright (dark) small balls, respectively.

bell, respectively. These results suggest that the $\langle 100 \rangle$ oriented CBI pair has the lowest energy and thus is the most stable dumbbell orientation. We find the neutral charge state to be most stable at midgap, followed by the negative (0.05 eV higher) and positive (0.67 eV higher) ones.

Kinetically, there are two ways to form C–B split interstitials, $BI + C \leftrightarrow CBI$ and $CI + B \leftrightarrow CBI$. Therefore, there are two sets of references to calculate the binding energies of the CBI pair. For the first process, we find as binding energy for the lowest-barrier decay process (the superscripts indicate charge states; e is an electron) at midgap $E_b(C^0 + BI^+ + e^- \leftrightarrow CBI^0) = 2.35$ eV. For the second process, we find (h is a hole) $E_b(CI^0 + B^- + h^+ \leftrightarrow CBI^0) = 1.11$ eV.

Capaz *et al.* have identified two types of C_2I clusters in Si.¹⁵ In the “type A” configuration, a C–I split interstitial is slightly perturbed by a nearby substitutional carbon. The “type B” configuration consists of a Si bond interstitial between two substitutional carbon atoms. However, since we found that for BCI and B_2I clusters, a $\langle 100 \rangle$ dumbbell configuration has the lowest energy, we also tried this structure for the C_2I cluster and found its energy to be lower than the two Capaz structures by 0.2 eV or more for all charge states. The binding energies calculated for the C_2I $\langle 100 \rangle$ dumbbell (the negative charge state is 0.11 (0.19) eV lower than the neutral (positive) one) as well as for the B_2I cluster¹² at midgap are $E_b(CI^0 + C^0 \leftrightarrow C_I + h^+) = 1.39$ eV and $E_b(BI^+ + B^- \leftrightarrow B_2I^0) = 1.49$ eV.

Despite the efforts to understand the mechanisms for the effect of the presence of carbon on the reduction of boron diffusion,^{1,3} some questions about the physical nature of TED suppression are still open. As an example, we want to mention the simulations of B and C diffusion in Si by Rücker *et al.*¹⁶ They found that the existence of C-rich clusters—whose composition, however, they did not identify—could remedy the discrepancy between their modeled and measured I undersaturation, which was predicted one order of magnitude larger than that found experimentally.¹⁶ Furthermore, our *ab initio* results open the possibility that CBI pairs form in addition to the one-species clusters and thus influence the annealing behavior, e.g., by reducing the population of mobile B in Si and therefore directly reducing B diffusion. We want to examine this influence, especially in competition with the C–I interactions, in the following in comparison to the experiment.

Experimental test structures were grown at temperatures between 500 °C and 650 °C by a reduced-pressure chemical vapor deposition epitaxial reactor. As seen in Fig. 2(a), the C profile is flat as deposited, whereas the B profile is confined in a very narrow region. The test structures also contained a

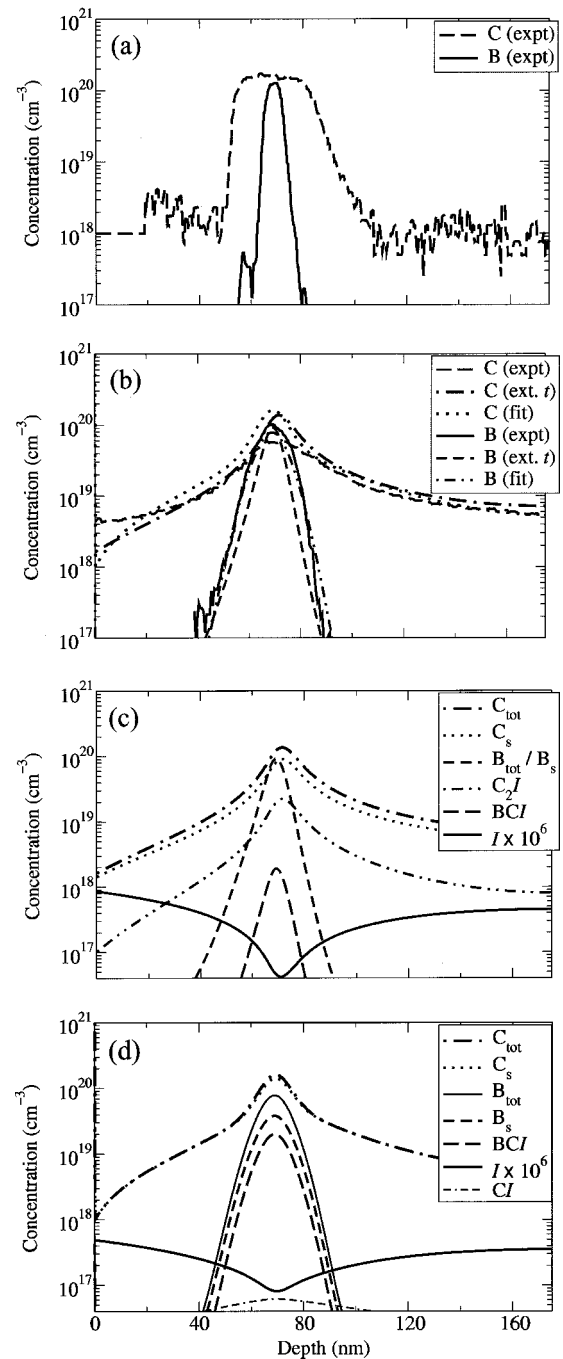


FIG. 2. (a) As-deposited experimental concentration profiles for boron and carbon, which also serve as initial profiles for the continuum simulations. (b) Experimental and simulated profiles for the total boron and carbon concentrations after an annealing step at 1042 °C for 20 s. (c) and (d) different contributions to the simulated total boron and carbon profiles shown in (b).

small concentration of Ge. After rapid thermal annealing at 1042 °C for 20 s, the peaks in the C and B concentration profiles are found at the same location, although C has diffused significantly as indicated by the broadening of the C profile [Fig. 2(b)].

In order to understand this behavior and to test our calculations, we combined our results into a continuum model. We started from a four-stream model for B diffusion and clustering,¹² in combination with the *ab initio* results of Ref. 7 for B diffusion and Ref. 17 for point-defect migration energy and prefactors. All reactions used in the model are indicated in Table I and have been formulated in the diffusion-

TABLE I. Energy values and other data found for the different defects.

Defect	Reaction	E_b^{theor}	E_b^{expt}	E_m^{theor}	E_m^{expt}
CI^0	$\rightarrow \text{I}^0 + \text{CI}^0$	1.75	1.63 ^a	0.56	0.73–0.88 ^b
BI^+	$\rightarrow \text{I}^{++} + \text{B}^-$	0.8 ^c	N/A	0.48 ^c	0.6 ^d
C_2I^-	$\rightarrow \text{CI}^0 + \text{C}^0 + e^-$	1.39	N/A
B_2I^0	$\rightarrow \text{BI}^+ + \text{B}^-$	1.49 ^e	N/A
CBI^0	$\rightarrow \text{BI}^+ + \text{C}^0 + e^-$	2.35	N/A
CBI^0	$\rightarrow \text{CI}^0 + \text{B}^- + h^+$	1.11	N/A

^aSee Ref. 11.^bSee Refs. 10 and 11.^cSee Ref. 7.^dSee Ref. 18.^eSee Ref. 12.

limited formalism. The model has been applied to a model structure with the B and C concentrations from Fig. 2(a) without the Ge. Our diffused distribution for B and C [Fig. 2(b), 1042 °C, 60 s (we used an extended time since our model without Ge and without further calibration of the *ab initio* numbers and initial conditions underestimates C diffusion)] looks very similar to experiment. We find the strong broadening of the C concentration profile to be due to the significantly higher binding energies of the CI pairs over BI [Fig. 2(c)]. Our model indicates that the major reason for the peaking of the C concentration is an undersaturation of self-interstitials in the area of the original C maximum due to the formation of mainly C_2I clusters, to a lesser degree of BCI clusters. Nevertheless, our model predicts BCI clusters to be the second-most important cluster in this setup, with a postanneal peak concentration $\sim 8\%$ as high as the C_2I peak.

After this, we used a Genetic Algorithm¹² to recalibrate the clustering parameters to experimental data for C and B–C codiffusion [Fig. 2(b)]. The resulting proprietary parameters indicate that for the calibrated model, the BCI cluster suddenly plays the strongest role, while C_2I is severely weakened [Fig. 2(d)]. This discrepancy between *ab initio* calculation and recalibration is probably caused by the choices for the other parameters in the four-stream model and the boundary conditions.

There is one important difference between the experiment and simulation that indicates a still incomplete modeling picture. Whereas B and C peak at exactly the same location in experiment, the simulated peaks are slightly shifted due to an initial shift in the centers of the as-deposited C and B distributions [Fig. 2(b)]. There are several possible explanations for this: first, this might be simply due to errors in the secondary ion mass spectroscopy (SIMS) measurements, although we have tried to maximize our resolution and minimize the error in the relative depth shift of the B versus C profiles. Specifically, we have first measured B and C distributions separately, using a Cs^+ primary beam with negative secondary ion collection (for accurate profiles), and then simultaneously, using an O_2^+ primary beam with positive secondary ion collection (for accurate depth lineup). However,

if this were not the case, the shifted B versus C peak in the simulation could be an indication of the dominance of BCI clusters (in contrast to our uncalibrated model). It also could suggest a stress-compensation effect (B and C cause compressive, Ge tensile stress) that is not captured in our model. A simple experiment without Ge and with simultaneous measurement of (possibly shifted) B and C concentrations could clarify this point further. Finally, we should mention that Kimerling *et al.*^{19,20} have conducted a series of deep-level transient spectroscopy studies involving samples of controlled boron, oxygen, and carbon content in Si. They suggested that C–B complex clusters exist when both C and B are present in Si, in agreement with our results.

In conclusion, our model qualitatively predicts experimental findings for a similar SiGeC structure reasonably well, which suggests strong C diffusion, nearly immobile B, and formation of a peak in the C concentration. Our model finds the BCI cluster to be the second-most important cluster after C_2I clusters for the examined concentrations and conditions.

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