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Fluorine in Si: Native-defect complexes and the suppression of impurity diffusion

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The transient enhanced diffusion of acceptor impurities severely affects the realization of ultrahigh doping regions in miniaturized Si-based devices. Fluorine codoping has been found to suppress this transient diffusion, but the mechanism underlying this effect is not understood. It has been proposed that fluorine-impurity or fluorine–native-defect interactions may be responsible. Here we clarify this mechanism combining first-principles theoretical studies of fluorine in Si and purposely designed experiments on Si structures containing boron and fluorine. The central interaction mechanism is the preferential binding of fluorine to Si-vacancy dangling bonds and the consequent formation of vacancy-fluorine complexes. The latter effectively act as traps for the excess self-interstitials that would normally cause boron transient enhanced diffusion. Instead, fluorine-boron interactions are marginal and do not play any significant role. Our results are also consistent with other observations such as native-defect trapping and bubble formation.

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I. INTRODUCTION

Si-based devices are the heart of modern microelectronics. The extreme miniaturization implied by their ultra-large-scale integration (ULSI) requires an extremely sharp spatial definition of dopant profiles. During the thermal processing involved in device fabrication, all commonly used dopants suffer from transient enhanced diffusion (TED).[1] In particular, it is now widely recognized[1,2] that the paradigmatic boron (B) acceptor diffuses efficiently in the presence of Si self-interstitials, which are generated during device processing to concentrations out of thermodynamic equilibrium. This is a serious hindrance to a sharp spatial definition of sub micron ultra-high-density dopant regions in Si devices.

Recently, it has been recognized[3,4] that fluorine (F) can be used to drastically suppress boron TED, although the origin of this effect is a matter of current debate.[3,5] Fluorine has also been reported to cause a trapping of native defects (e.g., produced by implant damage) drastically slowing down their recombination[6] and to induce the formation of bubbles and voids at high implant dose.[7] There are also recent reports of the observation of F-V complexes.[8] Therefore, an improved understanding of the microscopic mechanisms governing the behavior of F in Si, and its interaction with native defects and dopants, has basic and applicative importance in the key area of Si-based microelectronics.

In this paper, we present an extensive set of first-principles calculations on F and its complexes with native point defects and the B impurity, and custom-designed experiments (complementing earlier[3] results) studying the diffusion of B in thermal equilibrium (no excess self-interstitials) and of F in both equilibrium and nonequilibrium conditions. The results provide a rather complete picture of the physics of F in bulk Si. In particular, a microscopic mechanism for the suppression of self-interstitial-induced transient enhanced diffusion of B emerges naturally and consistently from our study. F preferentially forms complexes with Si vacancies V_{Si} (binding energy ~ 2 eV/atom) rather than with self-interstitials Si_i, with boron, or with itself (binding energy ~ 0.5-1 eV/atom). F forms such complexes during solid-phase epitaxy, producing vacancy-rich material. Self-interstitials Si_i released during annealing are captured by excess vacancies preferentially over B-self-interstitial pairing, thus preventing TED. F then diffuses efficiently as an interstitial. F-B, F-Si_i, and F-F coupling is marginal compared to that of vacancies and is therefore immaterial to TED. The same mechanism explains the drastic reduction of the B diffusion in the presence of a thermal-equilibrium Si_i concentration, of which we also report the direct observation. Finally, our results for F diffusion, F-native defect trapping, native-defect diffusion slowdown, and vacancy-interstitial recombination are consistent with recent experiments[6] and provide a framework for their interpretation.

II. METHODS

A. Theoretical

Defect geometries are determined according to total energies and forces calculated from first-principles within density functional theory in the generalized gradient approximation (GGA),[9] using the projector augmented waves (PAW) method[10] implemented in the VASP code.[11] All defects are simulated in 64-atom simple-cubic supercells of side equal to twice our calculated lattice parameter of Si, 5.46 Å. Defect formation energies are obtained[12] as $E_f = E_{\mathrm{tot}} - \Sigma_s n_s \mu_s + Q\mu_e$

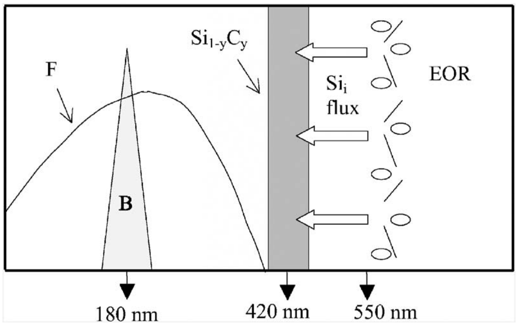

FIG. 1. Schematic description of the sample containing a $Si_{1-y}C_y$ layer ($y=0.03\%$). Upon post-SPE annealing, the Si_i emitted from the EOR region are trapped by the $Si_{1-y}C_y$ layer.

from the total energy E_{tot} of the defected supercell in charge state Q, the chemical potentials μ_s of the involved species, and the electronic chemical potential μ_e (which we generally refer to as the Fermi level.) The chemical potentials for F, B, and Si are determined by SiF_4, B_{50}, and bulk Si. We use ultrasoft[13] pseudopotentials[11] for Si and B and a PAW data set[11] for F (an admissible setup, as ultrasoft potentials are the spherical-projectors-only limiting case of PAW). Wave functions are expanded in plane waves, with cutoff at 280 eV. Brillouin zone summations use Monkhorst-Pack $4\times4\times4$ grids. For charged defects, the correction of Ref. 14 is included. Increased cutoff and cell size in selected tests results in negligible changes in the results. Error bars on formation energies are of order ±0.1 eV (e.g., see Ref. 15). Migration energies were extracted from minimum-energy paths generated between two given configurations with the nudged elastic band (NEB) method[16] as implemented in VASP.[11] All calculations are done at zero temperature. In all cases, the symmetry is deliberately kept lower than the "natural" or expected one.

B. Experimental

To study experimentally the effect of F in Si, we grew several custom-designed samples by molecular beam epitaxy (MBE) on a 5 in., (2×1) reconstructed Si (100) substrate.[3] The sample depicted in Fig. 1 contains a 50 nm thick carbon-enriched layer (C concentration 1.5×10^{20} cm^{-3}) at a depth of 420 nm, and a δ-doping B layer inserted at a depth of 180 nm (peak B concentration $\sim2\times10^{18}$ cm^{-3}, full width at half maximum $\sim$8 nm). Other reference samples were grown without the B δ layer and/or C-enriched layer. The samples were amorphized from the surface to a depth of $\sim$550 nm by implanting Si ions (3×10^{15} ions/cm^2 at 250 keV plus 2×10^{15} ions/cm^2 at 40 keV) at liquid nitrogen temperature. The amorphized samples were then enriched in F by implantation, with a fluence of 4×10^{14} ions/cm^2 at 100 keV. The implant energy was chosen[17] so that the F profile overlaps the B spike. Some of the amorphized samples were not implanted with F, so that they could be used as reference samples. To induce solid phase epitaxy (SPE), all the amorphized samples were annealed, in N_2 controlled atmosphere, at 450 °C for 30 min and subsequently at 700 °C for 120 min, taking into account the decrease of the SPE velocity caused by F and C.[18] Rutherford backscattering spectrometry (RBS), in channeling and random geometry, proved the high crystalline quality of the regrown layers.

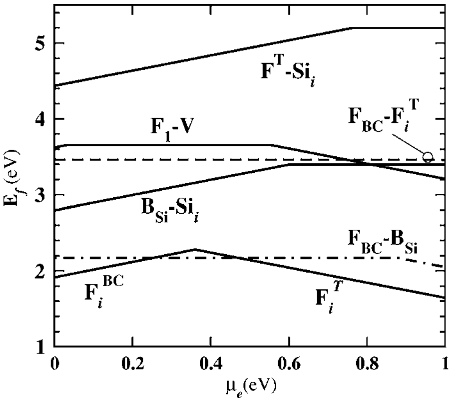

FIG. 2. Formation energies of the most relevant complexes. The local slope is the charge state, and the points of slope changes are the thermal charging levels.

As usual, the amorphizing implant induces at the end of the implant range a defect-rich region, called end-of-range (EOR) region, which acts as a source of self-interstitials (Si_i) during the post-SPE annealing.[19] The regrown samples were indeed treated by rapid-ramp thermal anneals (850–950°C for 10 min) to induce a release of Si_i from the EOR region. In the C-doped sample, the backflow of such Si_i's is suppressed by the C-rich silicon layer,[20,21] allowing us to study the F and B behavior in thermal condition for Si_i and vacancies V_{Si} concentrations. The chemical concentration depth profiles of F, B, and C were obtained by secondary-ion-mass spectrometry (SIMS), using a Cameca IMS-4*f* instrument, with a 3 keV O_2^+ analyzing beam, while collecting F^+, B^+, or C^+ secondary ions.

III. RESULTS

A. Theory

The theoretical results discussed here concern a selection of the most relevant among the numerous configurations of the fluorine–boron–self-interstitial–vacancy (F-B-Si_i-V_{Si}) system that we considered. These, however, turn out to be sufficient to set up a consistent picture of the suppression of boron TED in Si (see below). The μ_e-dependent formation energies of the relevant defects are displayed in Fig. 2. In Figs. 3 and 5, we depict the structure of a selection of F-Si_i-B and F-V_{Si} complexes, respectively. Figure 4 reports the binding energy of the relevant complexes, i.e., the difference in formation energy between a given complex and its separate constituents. This quantity is μ_e dependent because such are the individual formation energies. In our convention, negative values mean bound complexes.

Concerning the accuracy of the standard correction for charged defects used here (Ref. 14, see recent discussions in Ref. 22), we note that if the correction were removed entirely, the energies of singly charged centers in Fig. 2 would shift down by 0.15 eV, which entails minor changes. As to the binding energies discussed below (Fig. 4), the maximum

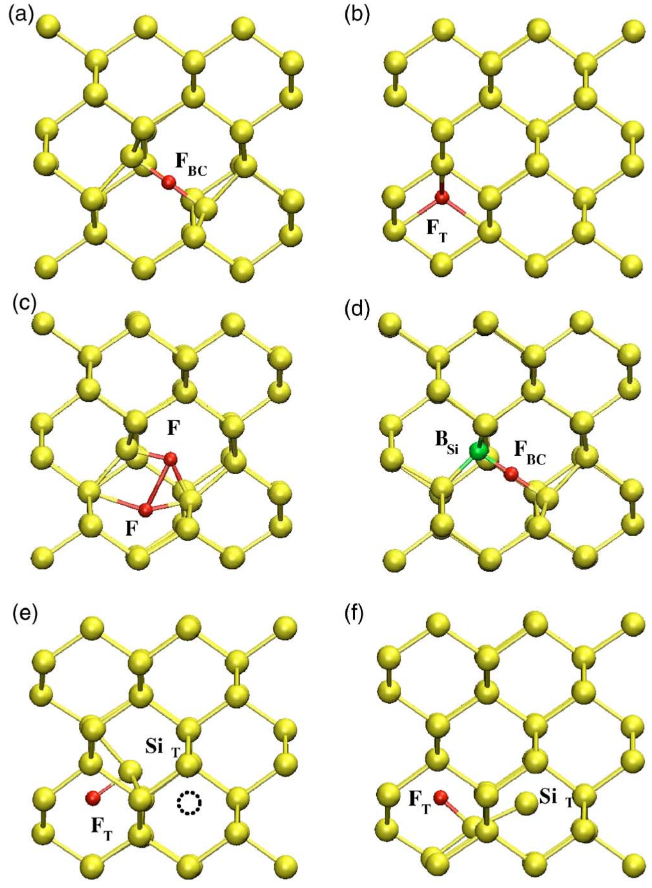

FIG. 3. (Color online) Structure of relevant F-involving defects: (a) bond-center interstitial F, (b) tetrahedral interstitial F, (c) F-F pair, (d) F-B pair, (e) first-neighbor F-Si$_i$ pair, (f) second-neighbor F-Si$_i$ pairs. The formation energies of defects (a)–(e) are in Fig. 2; defect (f) is 0.1 eV above defect (e) for all μ_e.

change in binding energy would be less than 7% for F-V complexes, again leaving all conclusions unaltered.

We also mention that while the formation energies depend on the chemical potentials of the species involved, the binding energies of the complexes discussed below (particularly Fig. 4), and the conclusions based thereupon, are unaffected. The choice of SiF$_4$ as a chemical potential reference is not unique, but is a reasonable mimic of a F atom at surface Si dangling bonds, which are likely drains for F.

Finally, the value of 1 eV for the gap in Figs. 2 and 4 is used for graphical clarity only. This value is close to both the experimental gap at room temperature (1.1 eV) and to the theoretical gap obtained from energy-difference calculations (1.1 eV) as explained in Ref. 15, Sec. III D and references therein.

1. Interstitial F

There are two competing ground-state configurations for interstitial F in Si. The bond-center-like F_i^{BC} interposes between adjacent Si atoms forming with them two covalent σ bonds. By electron counting, it must clearly release one electron to the crystal, and is therefore positively charged for most μ_e, as shown in Fig. 2. Its structure is in Fig. 3(a). The near-tetrahedral F_i^T [Fig. 3(b)] is negatively charged (Fig. 2) for almost all μ_e, because it captures an electron to complete its outer shell. These two configurations are a negative-U system whose accompanying lattice distortion is actually a site change (see Figs. 2 and 3). Concerning migration, for μ_e above about 0.35 eV, F_i^T has the lowest energy and it can travel through the hex site with a barrier of 0.60 eV without changing the charge state (as reported in Ref. 23). Alternatively, it may go through the F_i^{BC} configuration releasing two electrons, similarly to the Bourgoin-Corbett interstitial self-diffusion.[24] A specular reasoning applies to F_i^{BC} for μ_e below 0.35 eV, with two electrons being transiently captured instead. The migration then occurs between BC sites through T for μ_e below 0.35 eV and between T sites for μ_e above 0.35 eV. A lower bound for the μ_e-dependent migration energy for BC-T-BC or T-BC-T motion is the T-BC energy difference as shown in Fig. 2, namely $|0.7\text{ eV}-2\,\mu_e|$, i.e., 0.35 eV at midgap, and zero at the crossing point $\epsilon(+/-)$. This is consistent with the observation of fast stand-alone diffusion of F in Si (see below).

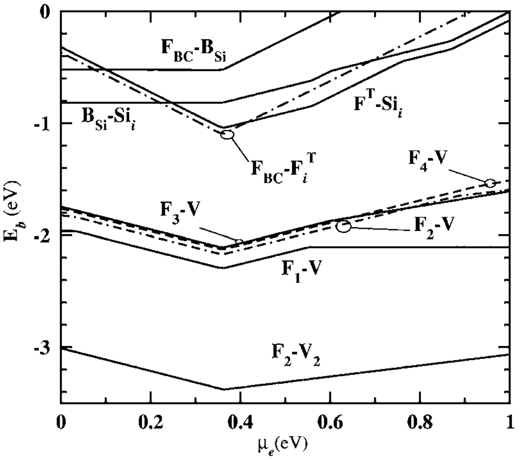

FIG. 4. Binding energies (per pair, or per F atom for multi-F complexes) of several relevant complexes, referred to separate constituent defects. Here the binding energy of F$_2V_2$ is referred to isolated V's and F's. If a divacancy (which has a binding energy of 1.45 eV) is assumed to form prior to F binding, the binding energy per F atom is reduced accordingly to about 2.5 eV at midgap.

2. F-F and F-B interaction

Being negatively charged, F_i^T's repel each other. F pairs can still form as the "F_i^T-F_i^{BC}" complex depicted in Fig. 3(c). This complex is bound by 1 eV at most, as can be seen in Fig. 4, which displays the binding energies of the various complexes. More interestingly, negative F_i^T and B$_{Si}$ repel each other strongly in general, and the only F-B bound complex is a F_i^{BC}-B$_{Si}$ pair [Fig. 3(d)], with F sitting in a B$_{Si}$-Si bond. The maximum binding energy of this complex is 0.5 eV (see Fig. 4), smaller than that of the B-Si$_i$, F-Si$_i$ (Sec. III A 3), and F-F complexes. As to TED suppression, F-F and F-B pairs are less, or at most, as bound as B-Si$_i$ pairs, as can be seen in Fig. 4. Hence, these complexes cannot prevent the pairing of Si$_i$ to B which causes TED.[1,2] Therefore, F-B interaction cannot be responsible for TED suppression.

3. F-Si$_i$ *complexes*

The most stable Si$_i$-F$_i$ complex, depicted in Fig. 3(e), is a Si$_i^T$-F$_i^T$ positively charged pair. It results from the respective doubly positive and singly negative charge of Si$_i^T$ and F$_i^T$ (neither sits exactly at a *T* site). The Si-F bond is 1.81 Å long. As can be seen in Fig. 4, this complex is only bound by ~1 eV compared to separated components. Thus, the result is that F-Si$_i$ pairs are only marginally more bound than B-Si$_i$ pairs; therefore, they cannot prevent the pairing of Si$_i$ to B, which causes TED.[1,2] As we will see below, the key to TED suppression is an indirect effect on self-interstitials due to F pairing with vacancies.

Before moving to that, we note that a possible first step in the motion of the F-Si$_i$ complex just discussed is a displacement of the Si$_i^T$ to a near-T site [dotted circle in Fig. 3(e)] second-neighbor to F. Our calculated energy barrier of 1.4 eV is a lower bound for its migration energy; notably, this is much larger than the migration barriers of either isolated F and isolated Si$_i$ in intrinsic conditions (both ~0.3 eV). This leads to a mutual trapping of F and Si$_i$ (see below).

Interestingly, the displacement just mentioned does not dissociate the pair, but rather results in the formation of a new complex, only 0.1 eV higher in energy. The structure of this complex is depicted in Fig. 3(f). The same F-Si$_i^T$ second-neighbor configuration is also found as the relaxed final state for F$_i^T$ attaching sideways to a dumbbell self-interstitial. In this complex, F couples strongly to a lattice Si, with a bond length of 1.71 Å, while the self-interstitial is in a configuration similar to that of the standard acceptor–self-interstitial complex.[2] This stability is unsurprising *a posteriori*, because the tightly bound lattice Si-F pair is negatively charged, and binds the Si$_i$ roughly as an acceptor would, and the complex as a whole is singly positive. Finally, note that the similar binding energy of these two pairs imply that F has a large capture or interaction basin for self-interstitials (via the second-neighbor or first-neighbor pairs).

4. F-V$_{\mathrm{Si}}$ *complexes*

Vacancy-fluorine complexes are by far the most stable among those investigated. As shown in Fig. 4, F$_n V$ single vacancy complexes are bound by up to over 2 eV per F atom compared to a vacancy and *n* isolated F interstitials. The most stable in all doping conditions is F$_1 V$. In all cases, each F binds to a single dangling bond. The typical resulting Si-F distance is ~1.7 Å. In complexes involving multiple F atoms in a single vacancy, F-Si bonds rotate away from the original dangling-bond direction in order for F's to avoid each other in the vacant site region. A clear example of this behavior is the structure of F$_3 V$, shown in Fig. 5(a). This mutual avoidance is expected, because each Si is at 2.35 Å from the vacant site, and the sum of the typical Si-F bond length and the F covalent radius is 2.4 Å, so there is no room available near the vacant site for more than one dangling-bond-oriented Si-F bond.

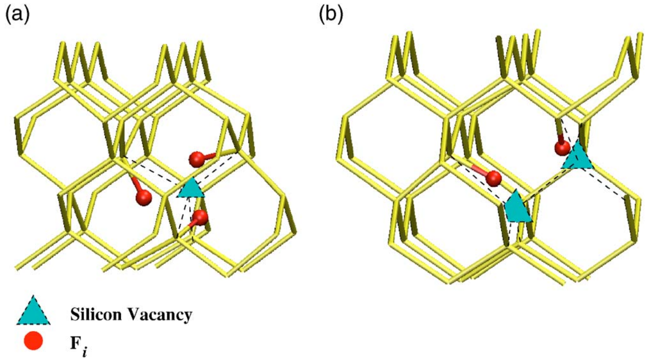

FIG. 5. (Color online) The structure of the F$_3 V$ and F$_2 V_2$ complexes.

Although the binding energies are similar for all F$_n V$ single vacancy complexes, F$_1 V$ is the most bound among them. Therefore, we only considered F$_2 V_2$ among multivacancy F complexes (and defer a more detailed analysis of F$_n V_m$ complexes to a forthcoming paper), which is sufficient for the present purposes. The F$_2 V_2$ structure in Fig. 5(b), shows a moderate F-Si bond rotation, which is consistent with our above discussion. The binding energy per F atom in this complex is well in excess of 3 eV compared to separated components. Thus, multivacancy F complexes are likely at high F doses. This is consistent with the observation of bubble formation under high F-dose irradiation.[6,7]

Although F-*V* complexes are highly stable, one expects that, if bulk Si is to remain stable in the presence of F, self-interstitials injected in the sample should recombine exothermally with the F-*V* complexes; and conversely, these complexes should not form spontaneously in the presence of F. From the data just presented, we calculate the energy gain upon recombination of F$_n V$ and a self-interstitial with ensuing emission of interstitial F, finding (for the Fermi level at midgap) 5 eV, 3.2 eV, and 1.5 eV for $n=1$, 2, and 3, respectively, which are positive (i.e., exothermal) as expected.

For $n=4$, however, the gain is negative (−0.8 eV), and therefore, F$_4$V would appear to be stable even in the presence of self-interstitials, and conversely to form spontaneously from bulk Si in the presence of interstitial F. There are several possible solutions to this paradox. First, especially in self-interstitial supersaturation, F atoms emitted upon annihilation of F$_4 V$ are likely to bind to self-interstitials; given the F-Si$_i$ binding energy (Fig. 4) of 1 eV, the recombination gain becomes positive again, between about 0.2 and 3.2 eV depending on the number (one to four) of F's forming a F-Si$_i$ complex. Second, even neglecting F-Si$_i$ binding, the concurrence of four F's at a single *V*—hence the spontaneous formation of F$_4 V$—is not especially likely. Nevertheless, the prediction on F$_4 V$ is consistent with the fact that if the F flux is extremely high, the formation of cavities and bubbles of mesoscopic size is indeed observed. (We note in passing that for F$_2 V_2$ the relevant transformation energy is that into F$_2 V$, which is again positive, 4.5 eV; the same is expected for larger F/*V* ratios, e.g., F$_6 V_2$,[25] which should transform into stable F$_4 V$+F's).

Besides the F-*V* complex being energetically favorable, the capture of vacancies by F does not appear to be kinetically hindered. For instance, a F$_i^{\mathrm{BC}}$ binds a second-neighbor vacancy with no activation barrier. On the other hand, self-interstitials injected in a region containing F-*V* complexes will efficiently annihilate them. Indeed, F$_n V$/Si$_i$ recombina-

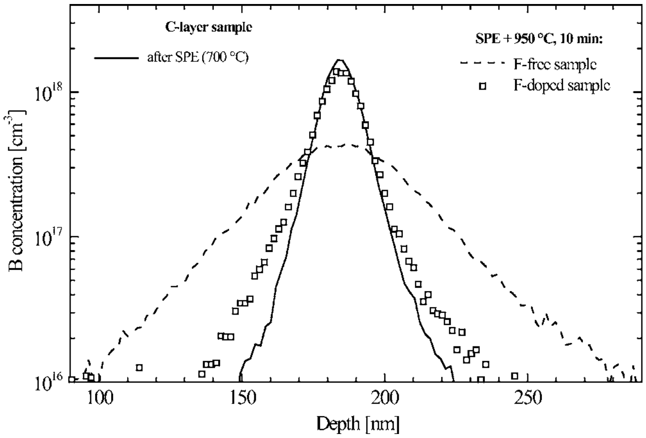

FIG. 6. Boron thermal diffusion profiles after SPE (continuous line) and after SPE plus the thermal annealing at 950°C for 10 min in the sample with F (open squares) and without F (dashed line).

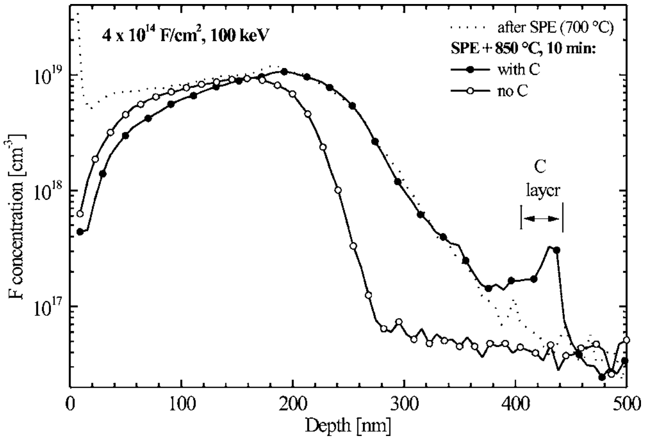

FIG. 7. F profiles after SPE (dotted line), after SPE plus the thermal annealing at 850°C for 10 min in the sample with (closed circles) and without (open circles) the $Si_{1-y}C_y$ layer.

tion with emission of F_i's is exothermic in all cases. In addition, we find a barrierless capture by F_1V of a self-interstitial from a first-neighbor T site. This suggests that there is no appreciable kinetic hindering by F against V-Si_i recombination.

As mentioned a F_i^{BC} second-neighbor to a vacancy captures it without barrier, and a F_1V complex is formed. One can envisage the converse process as a possible migration path for F_1V. From the energy difference of the two configurations mentioned, we can set an approximate upper bound of 2.1 eV to the migration of F_1V. In view of the simple structure of F_1V, its migration energy is presumably among the lowest of the various F-V complexes. We are currently investigating a concerted F-V motion that might lower this barrier; however, as F has to transiently detach from a dangling bond in any such concerted process, and the migration of F between two dangling bonds within the same vacancy has a barrier of 0.9 eV, we do not expect any major barrier reduction.

B. Experiments

F-induced suppression in nonequilibrium conditions has been experimentally demonstrated earlier, in particular by some of the present authors.[3] Here we complement those investigations studying the thermal equilibrium diffusion (TD) of B in the presence of F and the effects of the suppression of nonequilibrium Si_i from the EOR on the diffusion of F.

We studied the effect of fluorine on boron TD using the C layer sample schematized in Fig. 1. In Fig. 6, we report the B profile after SPE (solid line) as well as those after post-SPE annealing at 950°C for 10 min in the F-free sample (dashed line) and in the F-doped sample (4×10^{14} ions/cm^2 at 100 keV, open squares). Boron TD in the F-free sample is in good agreement with published data.[1] This confirms that the C-rich layer succesfully traps the flux of EOR self-interstitials. The thermal equilibrium diffused profile of B in the F enriched sample, shown as open squares in Fig. 6, clearly denotes a remarkable reduction of boron TD due to the presence of fluorine. We estimate that B diffusivity is reduced to 1/20 of the equilibrium value. It is important to underline that, after the post-SPE annealing at 950 °C, the fluence of F still present in the sample is about 30% of the implanted dose. Thus, we can state that F does efficiently suppress B diffusion in the presence of a thermal equilibrium concentration of self-interstitials.

As a second step, to clarify the diffusion mechanism of F, and in particular the effect of a Si_i excess flux, we studied the F diffusion in the presence of equilibrium and nonequilibrium concentrations of Si_i. We performed the post-SPE thermal treatment at 850 °C for 10 min, inducing the release of Si_i from EOR defects. The results are shown in Fig. 7. The dotted line represents the F profile after the SPE process. The open circles indicate the diffused F profile after post-SPE annealing in the case of a reference sample without the C layer (i.e., in Si_i supersaturation conditions). Finally, the closed circles display the F profile in the sample containing the C layer (i.e., in equilibrium conditions for the Si_i density).

A similar F out-diffusion toward the surface is observed in both cases, but major differences in profile shape and, especially, local concentration occur in the deeper region. In the sample without the C layer, a drastic erosion of the F profile occurred, which is consistent with a Fickian-deviated diffusion of F. These results clearly indicate an enhanced diffusion of fluorine in the presence of the Si_i flux, unequivocally demonstrating that the diffusion of fluorine is affected by the Si_i flux. The F accumulation at the C doped region (which may be ascribed to gettering by C-Si_i clusters) is two orders of magnitude below the peak concentration and therefore quantitatively minor.

IV. DISCUSSION

A. TED suppression

We now discuss the picture of B TED suppression by F which emerges from the theoretical results in connection with the experimental data in the preceeding Sec. III B, as well as with earlier experiments.[3] The results suggest F-V_{Si}

coupling as the dominant interaction of F in Si. F-Si$_i$ and F-B pairings are weaker, and closely competitive with TED-producing B-Si$_i$ pairing, so that they cannot produce such a definite effect as observed in experiment. The sequence of events we envisage is as follows.

(1) During SPE, F produces a vacancy-rich sample forming F-V complexes. This is consistent with the observed slowdown of SPE in the presence of F.[18] The excess of vacancies stored in the F-V complexes is not accompanied by an excess of self-interstitials, because in SPE there is no stoichiometry constraint, i.e., V_{Si} and Si$_i$ are not generated in pairs. No boron TED can occur at this stage, as vacancy-assisted diffusion of B is negligible (we calculate a B-V binding energy of only 0.5 eV and a barrier of 3 eV for B -V exchange).

(2) Upon post-SPE annealing, the self-interstitials released from EOR defects enter the B-containing region. Normally, TED would ensue. Due to fluorination, though, F-V complexes exist, which annihilate the Si$_i$'s by exothermal recombination. Recombination is fast because, as discussed earlier, barriers against recombination are absent or modest. V-Si$_i$ recombination is vastly favored energetically over B -Si$_i$ (as well as F-Si$_i$) pairing, and therefore, boron TED does not occur. F becomes interstitial and diffuses rapidly toward the surface, as is evident from Fig. 7.

(3) In thermal equilibrium, as discussed in Sec. III B (Fig. 6), the same as above applies except that each excess Si$_i$ is now generated thermally in pair with a V. The key point is that F produces vacancy enrichment during SPE, i.e., before thermal generation of V-Si$_i$ pairs.

In a hypothetical sample containing substitutional B, interstitial F, and no preexisting native defect, if no SPE would be performed, Si$_i$ and V would be thermally generated in pairs. Mobile interstitial F would then saturate all V's, and all Si$_i$'s would be left free to produce an enhanced diffusion of B.

(4) The experiments on F diffusion (Fig. 7) performed without a B spike and without a C-rich layer show fast F diffusion as Si$_i$'s emitted from the EOR enter the fluorinated region. In the presence of the C filter layer, F diffusion appears to be suppressed. Our data are consistent with these observations. In the first case, excess Si$_i$'s recombine with F-V complexes releasing F$_i$'s; these diffuse rapidly, having migration barriers around 0.4 eV in intrinsic conditions. In the second case, thermally generated Si$_i$ and V recombine in pairs, so that the highly stable SPE-generated F-V complexes continue to exist. F therefore can only diffuse as a F-V complex, whose migration energy is high (our estimate for F$_1V$ is 2 eV, experimental estimates[6] are around 2.2 eV).

In conclusion, theoretical results and the experiments described above, as well as those reported earlier,[3] enable us to conclude that F-V interactions are causing the TED or TD reduction of B. They are also fully consistent with the thermal equilibrium and nonequilibrium diffusion behavior of F in the absence of B.

Here we have dealt explicitly with self-interstitial-assisted TED. Because F has a larger binding (i.e., trapping) energy to vacancies than any dopant,[26] and in addition it suppresses vacancy motion drastically, its presence may interfere with vacancy-assisted enhanced diffusion as well, in the cases where this is relevant, e.g., for donors such as As or Sb in silicon. We are currently investigating this issue for Sb in Si.

B. Other experimental data

Our results indicate a definite preference of F for vacancies over self-interstitials and a highly favored formation of vacancy-F complexes. Recent positron-annihilation experiments[8] suggesting vacancy-fluorine complex formation are consistent with our predictions. The F/V ratio should be between 1 and 4 with a dominance of higher values (F$_4V$ is the most stable complex); in Ref. 8, an estimate was provided that two to three F atoms may typically surround the annihilation site. These data are consistent if one considers that annihilation may also occur at multivacancy complexes: e.g., our highly stable F$_2V_2$ has a F/V ratio of 1, but two F atoms near the double-vacant site. Indeed, it is quite reasonable to expect vacancy cluster ripening at a high F dose.[6,7] The tendency toward vacancy-F coupling is also consistent with the experimental observation of bubble and void formation at high implant doses of F.[7]

We have shown that the formation of highly stable F-V complexes results in severe vacancy trapping. This holds on energetic grounds, as the dissociation of F$_1V$ costs 2.5 to 3 eV depending on the Fermi level eV, as well as on kinetic grounds: indeed, the migration barrier of F$_1V$ is theoretically estimated in about 2 eV, whereas that of free vacancies is 0.5 eV; the motion of larger clusters will likely be no easier. Our migration barrier is also consistent with the experimental[6] estimates of 2.2 eV. In addition, recall that we found that F binds self-interstitials by 1 eV, and that a lower bound for the F-Si$_i$ complex migration energy is 1.4 eV. This results in a slowdown of self-interstitial migration, because a dumbbell self-interstitial has a migration barrier of 0.3 eV.[2,15] Therefore, the retarded Si$_i$-V recombination observed experimentally[6] is due to the formation of F-V and F-Si$_i$ complexes, and to the resulting (F-induced) effective slowdown of Si$_i$ and V diffusion. The higher migration barriers of the F-Si$_i$ and F-V complexes compared to those of interstitial F (0.4, 0.7, and 0.6 eV in intrinsic, p, and n conditions) imply that F diffusion is also suppressed by native-defect trapping, which is consistent with experiments.[3,6] We note in closing that V_{Si}-Si$_i$ recombination in itself is unhindered by F, as indicated by the barrierless recombination of a self-interstitial and the F$_1V$ complex with the emission of F$_i$.

In summary, we have presented a combined theoretical and experimental study of F in Si, with special reference to the F-induced suppression of the transient self-interstitial–mediated diffusion of acceptors. The results enable us to explain a number of recent observations such as vacancy-fluorine complexing, native-defect trapping, and boron TED suppression. They also provide a framework to understand F behavior in a general Si-based device environment.

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[1] P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989);N. E. B. Cowern, G. F. A. van de Walle, D. J. Gravesteijn, and C. J. Vriezema, Phys. Rev. Lett. **67**, 212 (1991).

[2] B. Sadigh, T. J. Lenosky, S. K. Theiss, M. J. Caturla, T. Diaz de la Rubia, and M. A. Foad, Phys. Rev. Lett. **83**, 4341 (1999);W. Windl, M. M. Bunea, R. Stumpf, S. T. Dunham, and M. P. Masquelier, *ibid.* **83**, 4345 (1999);M. Hakala, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **61**, 8155 (2000).

[3] G. Impellizzeri, J. H. R. dos Santos, S. Mirabella, F. Priolo, E. Napolitani, and A. Carnera, Appl. Phys. Lett. **84**, 1862 (2004).

[4] D. F. Downey, J. W. Chow, E. Ishida, and K. S. Jones, Appl. Phys. Lett. **73**, 1263 (1998).

[5] A. Mokhberi, R. Kasnavi, P. B. Griffin, and J. D. Plummer, Appl. Phys. Lett. **80**, 3530 (2002).

[6] X. D. Pi, C. P. Burrows, and P. G. Coleman, Phys. Rev. Lett. **90**, 155901 (2003).

[7] C. W. Nieh and L. J. Chen, Appl. Phys. Lett. **48**, 1528 (1986);C. H. Chu, J. J. Yang, and L. J. Chen, Nucl. Instrum. Methods Phys. Res. B **74**, 138 (1993).

[8] P. J. Simpson, Z. Jenei, P. Asoka-Kumar, R. R. Robison, and M. E. Law, Appl. Phys. Lett. **85**, 1538 (2004).

[9] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[10] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[11] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11169 (1996);G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).

[12] C. G. Van de Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, Phys. Rev. B **47**, 9425 (1993).

[13] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).

[14] M. Leslie and M. G. Gillan, J. Phys. C **18**, 973 (1985);G. Makov and M. C. Payne, Phys. Rev. B **51**, 4014 (1995).

[15] G. M. Lopez and V. Fiorentini, Phys. Rev. B **69**, 155206 (2004).

[16] H. Jonsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations* (World Scientific, Singapore, 1998);G. Henkelman, P. B. Uberuaga, and H. Jonsson, J. Chem. Phys. **113**, 9901 (2000).

[17] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Matter* (Pergamon Press, New York, 1985), Vol. 1.

[18] G. L. Olson and J. A. Roth, Mater. Sci. Rep. **3**, 1 (1988).

[19] K. S. Jones, R. G. Elliman, M. M. Petravic, P. Kringoj, Appl. Phys. Lett. **68**, 3111 (1996).

[20] S. Mirabella, A. Coati, D. De Salvador, E. Napolitani, A. Mattoni, G. Bisognin, M. Berti, A. Carnera, A. V. Drigo, S. Scalese, S. Pulvirenti, A. Terrasi, and F. Priolo, Phys. Rev. B **65**, 045209 (2002).

[21] E. Napolitani, A. Coati, D. De Salvador, A. Carnera, S. Mirabella, S. Scalese, and F. Priolo, Appl. Phys. Lett. **79**, 4145 (2001).

[22] J. Lento, J. L. Mozos, and R. M. Nieminen, J. Phys.: Condens. Matter **14**, 2637 (2002);U. Gerstmann, P. Deak, R. Rurali, B. Aradi, T. Frauenheim, and H. Overhof, Physica B, **340-342**, 190 (2003);J. Shim, E.-K. Lee, Y. J. Lee, and R. M. Nieminen, Phys. Rev. B **71**, 035206 (2005).

[23] C. G. Van de Walle, F. R. McFeely, and S. T. Pantelides, Phys. Rev. Lett. **61**, 1867 (1988).

[24] J. C. Bourgoin and J. W. Corbett, Phys. Lett. A **38**, 135 (1972).

[25] M. Diebel, S. Chakravarthi, S. T. Dunham, C. F. Machala, S. Ekbote, and A. Jain, *CMOS Front-End Materials and Process Technology* (Materials Research Society, Pittsburgh, 2003), D6.15.1, report F_3V to be lowest. No details are available on the calculation.

[26] Calculated binding energies of vacancies to donors and acceptors are between 0.2 and 1.4 eV: see, e.g., J. S. Nelson, P. A. Schultz, and A. F. Wright, Appl. Phys. Lett. **73**, 247 (1998);O. Pankratov, H. Huang, T. Diaz de la Rubia, and C. Mailhiot, Phys. Rev. B **56**, 13172 (1997);C. Melis, G. M. Lopez, and V. Fiorentini, Appl. Phys. Lett. **85**, 4902 (2004);P. Schirra, G. M. Lopez, and V. Fiorentini, Phys. Rev. B **70**, 245201 (2004).