

Formation and annealing of nitrogen-related complexes in SiC

U. Gerstmann, E. Rauls, Th. Frauenheim, and H. Overhof

Physics Department, Faculty of Science, University of Paderborn, D-33098 Paderborn, Germany

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We propose a mechanism for the annealing of vacancy-related defects in SiC, based on *ab initio* total energy calculations. Our mechanism is based on the formation and migration of carbon and nitrogen split interstitials resulting in $C_{Si}(N_C)_n$ or $V_{Si}(N_C)_n$ complexes as intermediate annealing products: In as-implanted samples, only recombination of nearby defects is possible, e.g., the disappearance of divacancies can be explained by a formation of $V_{Si}N_C$ pairs (*P12* centers). Dissociation of these very stable pairs at temperatures below 2000 °C is not possible. At elevated temperatures above 1000 °C, further aggregation becomes possible, resulting in electrically and optically inactive $V_{Si}(N_C)_4$ complexes. The recombination with carbon split interstitials, resulting in $C_{Si}N_C$ and $C_{Si}(N_C)_2$ donors, are discussed as competing processes.

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I. INTRODUCTION

In silicon carbide (SiC), the conventional thermal diffusion technique for doping is not practicable, as it requires very high temperatures above 1700 °C.^{1,2} Ion implantation is widely used instead, although this technique induces various intrinsic defects reducing the free charge carrier concentration. For further improvement of the SiC technology, an annealing of these defects is crucial, but hard to achieve.

Divacancies already vanish below room temperature, but an annealing of the isolated carbon vacancy (due to recombination with interstitials) requires temperatures up to 500 °C,³ whereas the annealing of the isolated silicon vacancy (V_{Si}) begins at temperatures above 750 °C and shows several annealing steps of rather uncertain origin. Additional annealing stages are found experimentally in the hexagonal polytypes near 1050 (Ref. 4) and 1400 °C,^{3,5} and have been tentatively explained by the dissociation of nitrogen-related complexes.

In this theoretical work we show that these additional annealing stages can not be identified with a dissociation of nitrogen-vacancy complexes. Instead, nitrogen and carbon split interstitials are shown to be mobile at temperatures above 800 and 1000 °C, respectively. Thus, further aggregation at the observed annealing temperatures is possible. When comparing our results with existing experimental data, we find strong indication for nitrogen-vacancy complexes to play an important role in SiC. Calculated total energies and hyperfine parameters lead to a new assignment of the so-called *P12* center in 6*H*-SiC (Ref. 6) to a silicon vacancy nitrogen pair ($V_{Si}N_C$) in C_{1h} symmetry. The formation of these $V_{Si}N_C$ pairs, calculated to be possible in as-implanted samples, explains the annealing of divacancies below room temperature. In addition, the fully nitrogen passivated vacancy $V_{Si}(N_C)_4$ turns out to be electrically and optically inactive. Therefore, this complex is an ideal candidate for a final, invisible annealing product of the silicon vacancy in SiC. Alternatively, the migration of $(CC)_C$ and $(NC)_C$ split interstitials can result in carbon antisite nitrogen pairs ($C_{Si}N_C$) or $C_{Si}(N_C)_2$ complexes. Both of them are shown to be donors with donor levels slightly below the conduction band.

This paper is organized as follows. In Sec. II, the computational methods are characterized. In Sec. III, the calculated hyperfine splittings of the *P12* spectrum in 6*H*-SiC and several possibilities to create nitrogen-vacancy pairs are discussed, ending up with a split interstitial based mechanism for the migration of N atoms. We also discuss a tentative correlation between calculated activation energies and annealing temperatures. Based on this we explain the different experimentally observed vacancy-related annealing stages with defect aggregation in the form of either $C_{Si}(N_C)_n$ or $V_{Si}(N_C)_n$ complexes.

II. COMPUTATIONAL

We used a combination of two methods within the framework of density functional theory (DFT). *Ab initio* total energy calculations were done using an extended version of the self-consistent linear muffin-tin orbital Green's functions method (LMTO)⁷ within the atomic spheres approximation (ASA).⁸ In this approach, the problem of an isolated impurity separates into two parts. The Green's function $g^0(E)$ of the perfect crystal is used to obtain the Green's function $g(E)$ of the impurity problem solving Dyson's equation

$$\{1 + g^0(E)[\Delta P(E) - \Delta S]\}g(E) = g^0(E). \quad (1)$$

Here ΔP is the perturbation of the potential function by the impurity while the matrix ΔS is the relaxation-induced change of the LMTO-ASA structure constants. From $g(E)$, total energies were calculated and minimized in order to find the geometry of the complexes. The solution of Eq. (1) in real space describes an isolated charged impurity in an otherwise perfect crystal, for which rather accurate charge transition levels are obtained.⁹ In addition, using the local spin density approximation (LSDA) and LMTO basis functions, the spatial distribution of the particle and magnetization densities is obtained, especially in the region near the nuclei. Therefore, it is possible to calculate accurate hyperfine interactions (HFI) of the magnetic moments of the electrons with that of the nuclei by using the relaxed atomic structures.¹⁰

The investigation of diffusion processes requires the use of the more flexible self-consistent charge density-functional based tight-binding (SCC-DFTB) method.¹¹ Most of the cal-

TABLE I. Observed HF parameters of the $P12$ center in $6H$ -SiC, and those calculated for the $V_{\text{Si}}\text{N}_{\text{C}}$ pair in $3C$ -SiC. Note, that for the negative silicon vacancy experimental EPR data give similar ligand hf interactions for different SiC polytypes (Ref. 25).

Defect	Symmetry	State	Atoms per C shell	^{13}C ($-1, -1, 1$) ligands		^{14}N ($1, 1, 1$) ligand	
				a	b	a	b
$P12$		Exp.		33.6	4.2	2.4	0.18
$V_{\text{Si}}\text{N}_{\text{C}}$	C_{3v}	2E	3	63.3	19.9	-1.5	-0.01
$V_{\text{Si}}\text{N}_{\text{C}}$	C_{1h}	2A_1	2	32.6	7.3	-1.6	0.26
			1	175.3	42.6		

calculations in $3C$ -SiC were performed in a $(3 \times 3 \times 3)$ -supercell containing 216 atoms. Starting from an initial structure, fully relaxed by a conjugate gradient scheme, the algorithm described in Ref. 12 is used to calculate the diffusion path into a previously calculated fully relaxed final structure. Thereby, for each process the saddle point geometry was found, from which we determine the energy barrier separating initial and final structure. For the description of interstitials and intermediate structures during a diffusion process only the atoms on the faces of the supercell have been fixed, while all other atoms were freely relaxed, since interstitials induce more extended lattice relaxations. The geometrical structure and the total energies of selected complexes have been checked by calculations in a supercell containing 512 atoms. For the calculations in the $6H$ polytype, a $(3 \times 3 \times 1)$ supercell containing 216 atoms has been used exclusively.

III. RESULTS

The incorporation of N atoms as shallow donors N_{C} does not lead to free charge carrier concentrations above $2 \times 10^{19} \text{ cm}^{-3}$.¹³ Obviously, for higher N concentrations nitrogen atoms form defect states that do not act as shallow dopants. N_2 dimers (the so-called A centers) are predominant N aggregates in diamond.¹⁴ In SiC, according to our calculations, this is not the case, as N aggregates are not stable against dissociation. For example, the total energy of the $\text{N}_{\text{C}}\text{N}_{\text{Si}}$ pair is about 1 eV higher than that of the dissociated constituents. N_{Si} induces a deep level in the gap at $E_{\text{C}} - 1.2$ eV and could be responsible for the saturation of the free charge carrier concentration. According to our calculations, though, an alternative structure $\text{C}_{\text{Si}}\text{N}_{\text{C}}$ is energetically favored by 4.5 eV with respect to N_{Si} and has a donor level close to the conduction band minimum. Thus, complexes with other, probably intrinsic, defects are a remaining possibility.

A. The $P12$ center in $6H$ -SiC — a $V_{\text{Si}}\text{N}_{\text{C}}$ pair

Nitrogen-vacancy complexes are prominent color centers in diamond,¹⁴ and there is strong experimental evidence for nitrogen-vacancy complexes in SiC, too: After neutron irradiation, Vainer and Il'in report an ESR spectrum ($P12$ center) in N-doped $6H$ -SiC.⁶ The resolved hyperfine structure of one ^{14}N nucleus and the additional splitting due to *three* equivalent carbon atoms suggest a nitrogen atom with a sili-

con vacancy on neighboring lattice sites in C_{3v} symmetry as a defect model. This, combined with an observed total spin of $S=1/2$ lead Vainer *et al.* to identify the defect with a neutral $V_{\text{Si}}\text{N}_{\text{C}}$ pair. Our LMTO total energy calculations confirm $V_{\text{Si}}\text{N}_{\text{C}}$ to be a stable defect pair with a binding energy of 2.4 eV. But as can be seen in Table I, the calculated hyperfine parameters do not even qualitatively correspond to the experimental data for this model. From our experience with hyperfine calculations for many similar defect systems [see, e.g., the isolated Si vacancy in $3C$ -SiC (Ref. 7)], we conclude that the large discrepancy, by a factor of 5 for the hyperfine interaction with a carbon ligand, e.g., strongly prohibits an identification of $P12$ with a neutral $V_{\text{Si}}\text{N}_{\text{C}}$ pair. Instead, we propose a reinterpretation of the spectrum in C_{1h} symmetry: For the neutral $V_{\text{Si}}\text{N}_{\text{C}}$ pair in C_{3v} symmetry, the fully occupied, nitrogen-related a_1 level is below the twofold degenerate e -orbital, which is occupied by one electron only. Due to this partial filling, the resulting 2E state is not stable against Jahn-Teller distortion lowering the symmetry of the defect to C_{1h} . According to our calculations, a slightly reduced outward movement of one of the three C ligands (about 5%, the other carbon ligands move outward by 7%) lowers the total energy by 0.06 eV. For the resulting 2A_1 defect state, the hyperfine splittings due to the *two* remaining equivalent C ligands (especially the isotropic part $a = 32.6$ MHz) agree with the experimentally observed values. The additional strong hyperfine interaction of $a=175.3$ MHz ($b=42.6$ MHz) is a result of the localization of the unpaired electron (a_1 orbital) at the prominent carbon ligand (see bottom of Fig. 1). For our interpretation to be applicable, this interaction must have been overlooked in the experiments. The line would be very weak, since the natural abundance of the carbon isotope ^{13}C ($I=1/2$) is only 1.1%. In addition, due to the three inequivalent sites in $6H$ -SiC, the linewidth of the signals with the large hyperfine interaction could be large enough to prevent a detection. Experimental investigation using ^{13}C enriched material should be able to detect the hyperfine splitting of the prominent carbon nucleus. Furthermore, our new interpretation of the $P12$ spectrum in $6H$ -SiC as a neutral $V_{\text{Si}}\text{N}_{\text{C}}$ pair in C_{1h} symmetry would require that there are two, not three, equivalent ligands with smaller hyperfine interaction.

B. $(\text{NC})_{\text{C}}$ split interstitials — mobile nitrogen in SiC

As already discussed in the literature, $V_{\text{Si}}\text{N}_{\text{C}}$ pairs can be formed by the migration of the Si vacancy. In a recent work,

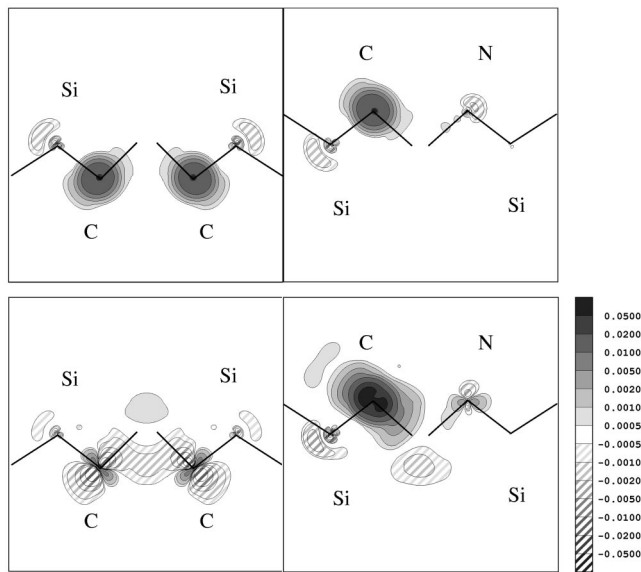


FIG. 1. Magnetization density (arb. unit.) of the neutral $V_{Si}N_C$ pair in C_{3v} symmetry (top) and in C_{1h} symmetry (bottom). In the right part the $(1\bar{1}0)$ plane containing the N ligand and one C ligand is given. The left part shows the two equivalent carbon ligands in the (110) plane.

however, we found the process of sublattice migration of V_{Si} to require 4.1 eV activation energy.¹⁵ Next to the N_C , this barrier is lowered to 3.5 eV, but pair formation at temperatures as low as 750 °C would be rather unlikely, as V_{Si} sublattice-migration according to recent EPR measurements is expected to happen at temperatures above 1600 °C.¹⁶ We thus have to consider a mechanism based on the migration of the N atoms instead.

Usually nitrogen atoms are built in as N_C on the carbon site in the SiC lattice. A migration process of N_C on the carbon sublattice, would consist of exchange processes between N and C atoms. As can be expected from former investigations of exchange processes in the SiC lattice, e.g., in case of antisites,¹⁷ the movement of N_C to the next carbon site costs about 12 eV—a value that is much too high to explain any migration of N. Interstitial based processes are expected to require lower activation energies.

The carbon split interstitial $(CC)_C$ (i.e., two carbon atoms sharing one carbon site, see Fig. 2) is created after ion implantation and has a rather low activation energy of 2.9 eV for sublattice migration.^{18,19} If a mobile $(CC)_C$ approaches an N_C , it can create $(NC)_C$ split interstitials: $(CC)_C + N_C \rightarrow (NC)_C$, see Fig. 2. The structure of the $(NC)_C$ split-interstitial is similar to that of $(CC)_C$:¹⁷ The N and the C atom share one C site and are both threefold coordinated, with their three bonds lying in planes perpendicular to each other. As in case of $(CC)_C$, the Si ligands are pushed outwards rather strongly, especially parallel to the defects axis. The change in energy during the process is shown in Fig. 2, with only 2.0 eV the $(NC)_C$ creation is even easier to activate than a migration of $(CC)_C$. The resulting structure $(NC)_C$ is 1.4 eV lower in energy than the initial structure.

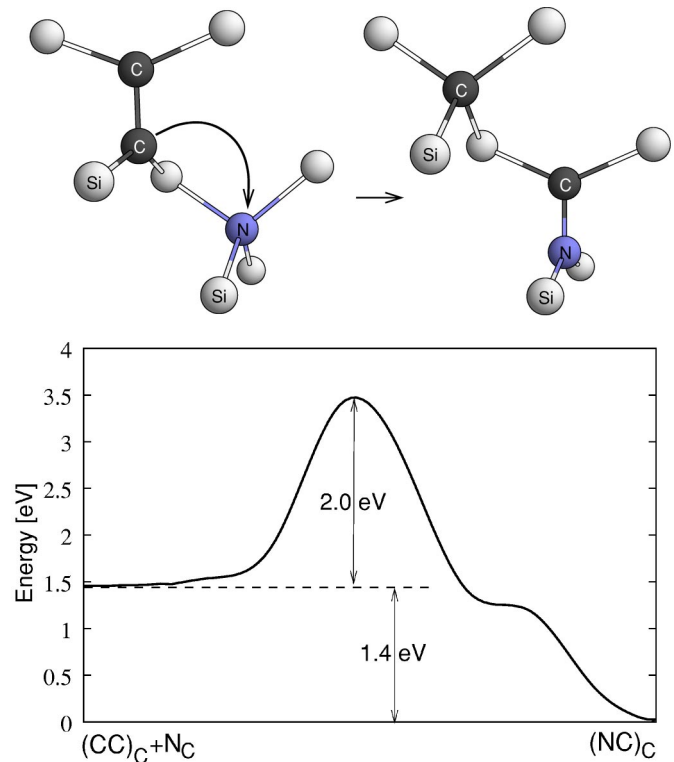


FIG. 2. A mechanism for the creation of mobile $(NC)_C$ split interstitials: one of the C atoms of a $(CC)_C$ split interstitial can move towards the N_C , resulting in a $(NC)_C$ split interstitial. In the energy diagram the activation energy (2.0 eV) and the energy gain (1.4 eV) in the final structure can be seen.

Once created, $(NC)_C$ split interstitials can migrate through the lattice. The activation energy for $(NC)_C$ moving to the next carbon site is with 2.5 eV even less than for the carbon split interstitial. A turn of the defect's orientation on its site (see Fig. 3), as required for directed diffusion, costs 0.8 eV [compare 0.6 eV for $(CC)_C$].

C. Formation of $V_{Si}N_C$ pairs

With $(NC)_C$ as a form of mobile nitrogen, there are several possibilities to create $V_{Si}N_C$ pairs. The most simple case is the recombination of $(NC)_C$ with divacancies $V_C V_{Si}$. We discuss two cases according to the orientation of the divacancy with respect to the split interstitial site. First, the

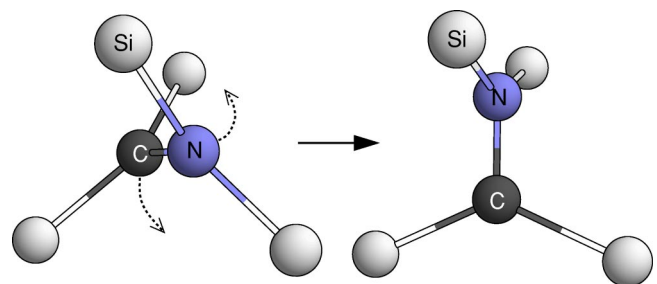


FIG. 3. As a split interstitial, $(NC)_C$ can exist in various orientations. Transforming from one to another orientation costs 0.8 eV activation energy.

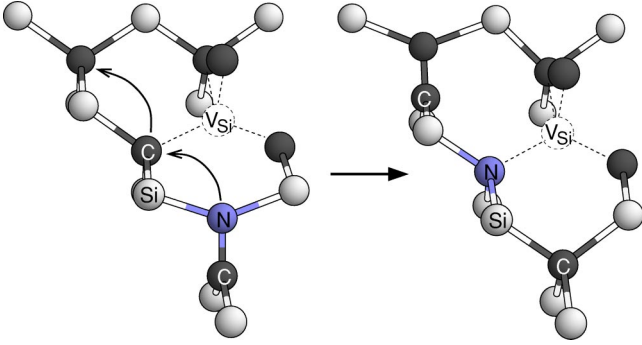


FIG. 4. A $(\text{NC})_C$ can kick out a carbon ligand of a silicon vacancy, resulting in a $V_{\text{Si}}\text{N}_C$ pair and a carbon split interstitial that can dissociate in a next step.

$(\text{NC})_C$ can approach the divacancy from the side of the V_C . Having come to a second neighbor distance, the N atom of the $(\text{NC})_C$ can move into the carbon vacancy with the very small activation barrier of 0.2 eV, creating a $V_{\text{Si}}\text{N}_C$ pair with an energy gain of 7.4 eV. Second, if the $(\text{NC})_C$ approaches the divacancy from the side of the V_{Si} , it fills up this site, forming a $\text{N}_{\text{Si}}V_C$ pair with an activation energy of 1.0 eV and an energy gain of 8.0 eV. This pair defect turns out to be only 0.8 eV higher in energy than the inverse $V_{\text{Si}}\text{N}_C$ pair. However, the activation energy for the nitrogen atom to move to the vacant carbon site has been calculated to be 2.5 eV, i.e., as high as the migration barrier of $(\text{NC})_C$ movement. Hence, under conditions when $(\text{NC})_C$ migration can be expected, this barrier can be overcome, resulting in the energetically favored $V_{\text{Si}}\text{N}_C$ structure.

There is another, somewhat surprising way to create a $V_{\text{Si}}\text{N}_C$ pair, if $(\text{NC})_C$ meets a silicon vacancy during its migration process. The vacancy can simply be filled up, resulting in a N_{Si} . However, our calculations show that the N atom of the split interstitial more likely substitutes one of the carbon ligands of the vacancy, while the carbon atom moves throughout the vacancy and forms a carbon split interstitial $(\text{CC})_C$ with one of the other ligands or with one of the third neighbor carbon atoms, as shown in Fig. 4. This reaction can be easily understood, since nitrogen in group-IV semiconductors prefers to be incorporated in threefold coordinated positions.²⁰ 2.9 eV are needed to activate this mechanism with a gain of 1.8 eV, see Table II. The resulting structure is a $V_{\text{Si}}\text{N}_C$ pair and a $(\text{CC})_C$ that can then dissociate and possibly mobilize further N_C on its way through the lattice. In this way, we get $V_{\text{Si}}\text{N}_C$ pairs and, in addition, N_C mobilization is sustained as long as N_C are present.

Alternatively, the N atom can push a C ligand to the Si site, resulting in a $\text{C}_{\text{Si}}\text{N}_C$ pair, which will be discussed more detailed in the following sections. This process requires only 2.0 eV activation energy and has to be regarded as a competing process to the $V_{\text{Si}}\text{N}_C$ creation.

D. Activation energies and annealing temperatures

In Table II we list the calculated migration mechanisms, their activation energies ΔE_{act} , as well as the energy gain of the final relaxed structure compared to the initial relaxed

TABLE II. Overview of the calculated migration mechanisms, activation energies, and energy gains. First the processes involving only a movement of V_{Si} , then the processes involving $(\text{CC})_C$ migration, finally the processes involving $(\text{NC})_C$ migration are listed. Barriers for the inverse processes can be obtained by adding the given energy barrier and the energy gain.

Initial structure	Energy barrier [eV]	Final structure	Energy gain [eV]
V_{Si}	4.1	$V_{\text{Si}}^{\text{next site}}$	-
V_{Si}	1.7	$V_C\text{C}_{\text{Si}}$	1.8
$V_{\text{Si}}+\text{N}_C$	3.5	$V_{\text{Si}}\text{N}_C$	2.0
$(\text{CC})_C$	2.9	$(\text{CC})_C^{\text{next site}}$	-
$(\text{CC})_C$	0.6	$(\text{CC})_C^{\text{turned}}$	-
$(\text{CC})_C+\text{N}_C$	2.0	$(\text{NC})_C$	1.4
$(\text{CC})_C+\text{C}_{\text{Si}}\text{N}_C$	1.8	$\text{C}_{\text{Si}}(\text{NC})_C$	1.9
$(\text{CC})_C+V_{\text{Si}}\text{N}_C$	1.9	$\text{C}_{\text{Si}}\text{N}_C$	9.7
$(\text{CC})_C+V_{\text{Si}}(\text{N}_C)_2$	2.4	$\text{C}_{\text{Si}}(\text{N}_C)_2$	7.5
$(\text{NC})_C$	2.5	$(\text{NC})_C^{\text{next site}}$	-
$(\text{NC})_C$	0.8	$(\text{NC})_C^{\text{turned}}$	-
$(\text{NC})_C+V_{\text{Si}}$	2.0	$\text{C}_{\text{Si}}\text{N}_C$	10.6
$(\text{NC})_C+V_C\text{C}_{\text{Si}}$	0.3	$\text{C}_{\text{Si}}\text{N}_C$	8.8
$(\text{NC})_C+V_{\text{Si}}\text{N}_C$	1.6	$\text{C}_{\text{Si}}(\text{N}_C)_2$	9.3
$(\text{NC})_C+V_{\text{Si}}$	2.9	$V_{\text{Si}}\text{N}_C+(\text{CC})_C$	1.8
$(\text{NC})_C+V_{\text{Si}}(\text{N}_C)_3$	2.9	$V_{\text{Si}}(\text{N}_C)_4+(\text{CC})_C$	2.0
$(\text{NC})_C+V_CV_{\text{Si}}$	0.2	$V_{\text{Si}}\text{N}_C$	7.4
$(\text{NC})_C+V_{\text{Si}}V_C$	1.0	$V_C\text{N}_{\text{Si}}$	8.0
$(\text{NC})_C+V_CV_{\text{Si}}(\text{N}_C)_3$	1.0	$V_{\text{Si}}(\text{N}_C)_4$	8.9
$V_C\text{N}_{\text{Si}}$	2.5	$V_{\text{Si}}\text{N}_C$	0.8

structure. Processes involving only a movement of V_{Si} are followed by processes involving $(\text{CC})_C$ migration and processes built upon $(\text{NC})_C$ migration. The barriers for the reverse mechanisms can be obtained by adding the given energy barrier and the energy gain. A comparison of our activation energies with available *ab initio* data (sublattice migration of vacancies, formation of the $V_C\text{C}_{\text{Si}}$ pair)¹⁹ suggests deviations up to ≈ 0.5 eV. Within our calculations the given energies define at least upper limits, if in spite of intensive search the saddle point configuration with the lowest energy should have been missed.

To correlate our results with the experimentally observed annealing behavior (the “disappearance” of defects), an identification of the calculated activation energies with a thermodynamic temperature is necessary. Unfortunately, due to several possible annealing processes (migration, recombination, complex formation, or dissociation), the interaction with other dopants, neglected entropic contributions, and varying annealing times, a simple unique assignment is not possible. However, using a simple Boltzmann distribution to describe the variation of the number of stable defects versus temperature, we obtain

$$T = \ln(\omega_D \tau) \frac{\Delta E_{\text{act}}}{k_B}, \quad (2)$$

where τ is the lifetime of the defects and ω_D denotes the Debye frequency in SiC ($\approx 1.6 \times 10^{13}$ 1/s). As a first approxi-

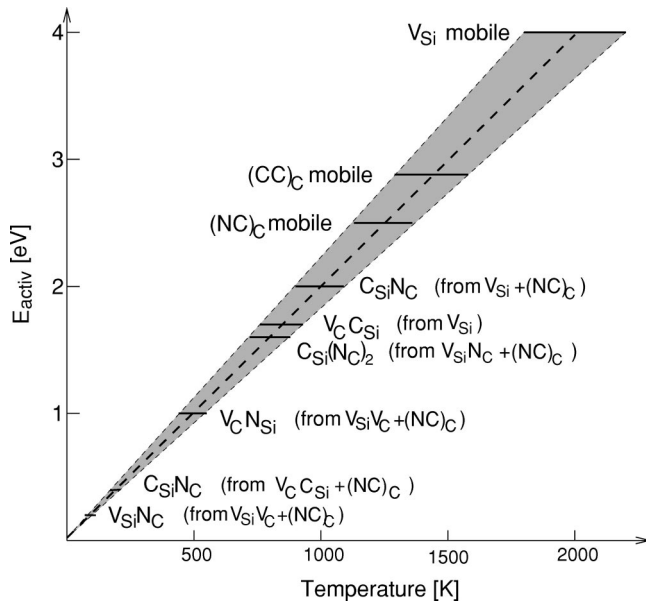


FIG. 5. Calculated activation energies are tentatively assigned to temperatures. The shaded region indicates a range of uncertainty that arises from effects as the vicinity of dopant atoms, or contributions of entropy.

mation we classify defects as “stable” if they exist at least 1 to 100 seconds in a given configuration. In most cases, the change in entropy ΔS between saddle point geometry and minimum energy structure can be expected to be positive.¹⁵ Therefore, the neglected entropical contributions $T \times \Delta S$ can be expected to lower the calculated activation barriers, an effect that becomes relevant especially at elevated temperatures. According to Eq. (2), a value of 500 K corresponds to an energy of 1 eV. Thus, the calculated activation energies ΔE_{act} can be assigned to a range of temperatures as indicated by the shaded region in Fig. 5.

We are now able to discuss our results in view of the experimentally observed findings. As mentioned above, the $(\text{NC})_{\text{C}}$ -nitrogen split interstitial is calculated to be mobile at a lowest temperature between 800 and 1000 °C. The corresponding carbon split interstitial needs temperatures above 1000 °C, whereas vacancy sublattice migration can be expected above 1500 °C. At annealing temperatures below 700 °C, only recombination of neighboring defects is possible. The rather low activation energies, found for the recombination of divacancies with nearby nitrogen (0.2 eV), could explain the presence of $V_{\text{Si}}\text{N}_{\text{C}}$ pairs in as-implanted material.⁶

E. Post-implantation annealing above 700 °C

Recently, Åberg *et al.*^{21,22} found that in N-doped 4H-SiC the reduction of the free charge carrier concentration upon additional ion implantation with H, He, Al, and B is compensated in part by post-implantation annealing above 700 °C. Full recovery of free charge carriers is observed around 1000 °C. The authors suggest the dissociation of implantation-induced nitrogen-related complexes as a first model with a dissociation barrier of 3.2 eV.²²

From the results discussed above a $V_{\text{Si}}\text{N}_{\text{C}}$ pair should be a good candidate for those complexes in as-implanted samples. Using the SCC-DFTB method, we have calculated several pair dissociation reactions. The lowest activation energy was found for the V_{Si} movement to the second neighbor site, which requires 5.5 eV (all mechanisms involving a movement of the N atom either on the sublattice or onto an interstitial site are even more costly in energy). An energy barrier of 5.5 eV, however, strongly contradicts a dissociation of this pair at realistic temperatures (see also Fig. 5). We thus have to consider further aggregation as an alternative possibility, as, e.g., $(\text{CC})_{\text{C}}$ or $(\text{NC})_{\text{C}}$ moving on the C sublattice.

In the last case the formation of $V_{\text{Si}}(\text{N}_{\text{C}})_n$ complexes would lead to a further passivation of nitrogen donors instead of a recovery of free charge carriers observed in the experiment. In fact, $V_{\text{Si}}(\text{N}_{\text{C}})_n$ complexes can be created by a subsequent addition of $(\text{NC})_{\text{C}}$ split interstitials to $V_{\text{Si}}(\text{N}_{\text{C}})_{n-1}$ complexes. Approaching the silicon vacancy of a $V_{\text{Si}}(\text{N}_{\text{C}})_{n-1}$ complex, one of the ligands can be kicked out, resulting in a $V_{\text{Si}}(\text{N}_{\text{C}})_n$ complex and a $(\text{CC})_{\text{C}}$ split interstitial. Our calculations for $n=1$ and $n=4$ show that neither the activation barriers nor the energy gain vary significantly with the number n of N atoms in the complex (see Table II).

When approaching a $V_{\text{Si}}\text{N}_{\text{C}}$ pair, $(\text{CC})_{\text{C}}$ carbon split interstitials can recombine, resulting in a $\text{C}_{\text{Si}}\text{N}_{\text{C}}$ pair. Only 1.9 eV are needed for this process, while 9.7 eV are gained compared to the initial structure, see Table II. This pair appeared already in the discussion of the kick-out process, but yet another mechanism is conceivable for the creation of the $\text{C}_{\text{Si}}\text{N}_{\text{C}}$ pair. As shown previously, the isolated silicon vacancy can transform into the $V_{\text{C}}\text{C}_{\text{Si}}$ pair^{17,23} with an energy gain of 1.6 eV and an activation energy of 1.7 eV. Consequently, many silicon vacancies may have transformed already at the temperatures in question, compare Fig. 5. If a $(\text{NC})_{\text{C}}$ split interstitial meets such a $V_{\text{C}}\text{C}_{\text{Si}}$ pair, the $\text{C}_{\text{Si}}\text{N}_{\text{C}}$ pair will be created with only 0.3 eV activation energy and an energy gain of 8.8 eV.

This $\text{C}_{\text{Si}}\text{N}_{\text{C}}$ pair has been calculated to have a donor level close to the conduction band minimum. As mentioned above, the activation of the $(\text{CC})_{\text{C}}$ to migrate through the 3C-SiC lattice requires an energy of 2.9 eV. According to Fig. 5, the formation of this pair could explain the full recovery of free charge carriers after post-implantation annealing at temperatures above 1000 °C. However, if there are mobile $(\text{NC})_{\text{C}}$ split interstitials left, the formation of $V_{\text{Si}}(\text{N}_{\text{C}})_n$ complexes remains a competing process.

F. The weak annealing stage around 1000 °C

Using capacitance spectroscopy, Ballandovich and Violina found three deep acceptor levels in 6H-SiC with energies at $E_{\text{C}}-0.35$ eV, $E_{\text{C}}-0.6$ eV, and $E_{\text{C}}-1.1$ eV, thermally stable up to 1050 °C.⁴ According to positron lifetime spectroscopy,³ the disappearance of these acceptor levels is correlated with a weak annealing stage for vacancy-related defects. According to our LMTO total energy calculations, the energies for the uppermost acceptor levels of $V_{\text{Si}}(\text{N}_{\text{C}})_n$, $n=1,2,3$ agree with the experimental data (see Table III).

TABLE III. Calculated energetic position in [eV] of the uppermost acceptor levels of the $V_{\text{Si}}(\text{N}_C)_n$ complexes with respect to the conduction band edge. Comparison with the experimental data in Ref. 4 shows nearly perfect agreement. Note, that the fully N-passivated vacancy $V_{\text{Si}}(\text{N}_C)_4$ turns out to be electrically inactive.

Defect	Transition	LMTO-GF	Exp.
$V_{\text{Si}}\text{N}_C$	-2/-3	-0.34	-0.35
$V_{\text{Si}}(\text{N}_C)_2$	-1/-2	-0.59	-0.60
$V_{\text{Si}}(\text{N}_C)_3$	0/-1	-1.17	-1.10
$V_{\text{Si}}(\text{N}_C)_4$			

Again, the most promising model is a recombination of carbon split interstitials $(\text{CC})_C$ with neighboring $V_{\text{Si}}(\text{N}_C)_n$ complexes forming $\text{C}_{\text{Si}}(\text{N}_C)_n$ complexes: The formation of a $\text{C}_{\text{Si}}(\text{N}_C)_2$ complex needs 2.4 eV activation energy, while 7.5 eV are gained. As in the case of the $\text{C}_{\text{Si}}\text{N}_C$ pairs, this complex is a donor with an occupation level close to the conduction band minimum, according to our LMTO calculations. The $\text{C}_{\text{Si}}(\text{N}_C)_3$ complex, however, dissociates into isolated N_C and $\text{C}_{\text{Si}}(\text{N}_C)_2$ donors with an energy gain of about 3 eV. The high stability of the $\text{C}_{\text{Si}}(\text{N}_C)_2$ complex is caused by an off-center relaxation of the central C atom and a strong inward movement of its two carbon neighbors (sp^2 hybridization with two strong double bonds), reducing this distance by 22% to a value of 1.47 Å, shorter than the nearest neighbor distance in diamond (1.54 Å). In contrast, the nitrogen atoms remain nearly at their ideal lattice sites. As it is shown in Table II, the $\text{C}_{\text{Si}}(\text{N}_C)_2$ complex can also be formed if an $(\text{NC})_C$ is located in the neighborhood of a $V_{\text{Si}}\text{N}_C$ pair. Only 1.6 eV are needed to activate a recombination process.

The recombination of acceptors $V_{\text{Si}}(\text{N}_C)_n$ with split interstitials would lead to shallow donors and, therefore, to a recovery process as observed in the experiments²² and to the disappearance of the acceptor levels⁴ around 1050 °C. At the moment, this part of the model is rather speculative—further EPR investigations with resolved hyperfine splittings due to carbon and nitrogen nuclei should be the key to overcome this problem. In Table IV, we give calculated hyperfine parameters (LMTO method) for all defect states with nonvanishing total spin S of the $V_{\text{Si}}(\text{N}_C)_n$ complexes. As experi-

mentally observed in case of the isolated Si vacancy, similar hyperfine splittings can be expected for different polytypes. The values for the cubic material should, thus, be a basic guide for future experimental work in all SiC polytypes.

G. Properties of $V_{\text{Si}}(\text{N}_C)_n$ and the strong annealing stage at 1400 °C

In addition to its neutral charge state already discussed above, there are two further charge states of the nitrogen-vacancy pair $V_{\text{Si}}\text{N}_C$ which give rise to an EPR-active defect state (see Table IV): In the negative charge state ($V_{\text{Si}}\text{N}_C^-$) the doubly degenerate e -orbital is occupied with two electrons. Therefore, no Jahn-Teller distortion takes place, in contrast to the neutral charge state. Thus, the C_{3v} -symmetry of the atomic configuration is conserved and a hyperfine splitting of $a=70.5$ MHz due to three equivalent carbon ligands is obtained. For $V_{\text{Si}}\text{N}_C^{2-}$ the occupation of the e orbital with three electrons leads to an inequivalent outward movement of one carbon ligand. The unpaired electron fills the upper a_2 -level whose nodal plain contains the nitrogen ligand and the prominent carbon ligand. Here, the hyperfine values nearly vanish and the spin density is localized at the two equivalent carbon ligands only ($a=143.1$ MHz, $b=27.3$ MHz).

Due to the C_{2v} -symmetry of the $V_{\text{Si}}(\text{N}_C)_2$ -complexes, there are only nondegenerate orbitals, and, thus, no need for Jahn-Teller distortions. The positive charge state 2A_1 shows the highest ${}^{14}\text{N}$ hyperfine values ($a=8.2$ MHz, $b=2.9$ MHz) among the $V_{\text{Si}}(\text{N}_C)_n$ complexes. For the negative charge state, the unpaired electron is localized in a b_2 orbital at the carbon ligands and, as a consequence, the ${}^{14}\text{N}$ hyperfine splitting is reduced to a value of -1.6 MHz, accompanied by strong splittings due to the two ${}^{13}\text{C}$ nuclei ($a=106.6$ MHz, $b=28.8$ MHz).

In comparison with the $V_{\text{Si}}\text{N}_C$ pair, the crystal field of the $V_{\text{Si}}(\text{N}_C)_3$ complex leads to the inverse term sequence of the upper a_1 and the lower e orbital. In its neutral charge state, these levels are occupied with five electrons, resulting in an $e^4a_1^1$ configuration. Again, Jahn-Teller distortions play no role, and the C_{3v} symmetry of the atomic arrangement is conserved. The fully nitrogen passivated silicon vacancy

TABLE IV. HFI of possible EPR-active, NV-related defect states in SiC. The calculated values are given for the 3C polytype. As for the negative silicon vacancy (Ref. 25) similar values for the hexagonal polytypes should be expected.

Defect	State			${}^{13}\text{C}$ (-1, -1, 1) ligands			${}^{14}\text{N}$ (1, 1, 1) ligands		
				a	b	b'	a	b	b'
$(V_{\text{Si}}\text{N}_C)^0$	2A_1	C_{1h}	$a_1^2 a_1^1 a_2^0$	32.6	7.3	0.12	-1.6	0.26	0.02
				178.7	43.9	0.57			
$(V_{\text{Si}}\text{N}_C)^-$	3E	C_{3v}	$a_1^2 e^2$	70.5	19.2	0.50	-1.6	-0.04	
$(V_{\text{Si}}\text{N}_C)^{2-}$	2A_2	C_{1h}	$a_1^2 a_1^1 a_2^1$	143.1	27.3	0.29	-1.3	0.16	0.09
				-2.9	0.7	0.53			
$[V_{\text{Si}}(\text{N}_C)_2]^+$	2A_1	C_{2v}	$b_1^2 a_1^1 b_2^0$	37.1	19.4	0.11	8.2	2.90	0.05
$[V_{\text{Si}}(\text{N}_C)_2]^-$	2B_2	C_{2v}	$b_1^2 a_1^2 b_2^1$	106.6	28.8	0.26	-1.6	0.15	0.09
$[V_{\text{Si}}(\text{N}_C)_3]^0$	2A_1	C_{3v}	$e^4 a_1^1$	141.0	50.8	0.50	-3.3	1.01	0.02

$V_{\text{Si}}(\text{N}_{\text{C}})_4$ turns out to be a very stable complex in SiC with a binding energy of 9.8 eV. Again, the nitrogen ligands are threefold coordinated and remain nearly at their ideal lattice sites, resulting in T_d symmetry. Moreover, the electronic structure of the complex is determined by a fully occupied t_2 level in the valence band. As a result, similar to the so-called B center ($V\text{-N}_4$)—the dominant defect in natural IaB diamond—this neutral defect is electrically and optically inactive. In analogy with comprehensive analysis in diamond²⁴ it should also be expected to be invisible with respect to positron annihilation. Thus, the formation of these complexes (activation energy above 3 eV) could explain the sharp increase in positron lifetime at 1400 °C.

In other words, the fully nitrogen passivated vacancy $V_{\text{Si}}(\text{N}_{\text{C}})_4$ is an ideal candidate for a final annealing product of the silicon vacancy in SiC, if assuming that some $V_{\text{Si}}(\text{N}_{\text{C}})_n$ survive the annealing steps between 700 and 1100 °C. Alternatively, it is possible that due to the very high temperatures dissociation of other complexes takes place. As a result, the annealing process could end up in one of the most stable complexes: The $V_{\text{Si}}(\text{N}_{\text{C}})_4$ with a binding energy of nearly 10 eV.

In addition, this complex can only hardly dissociate in its components: The process similar to the one discussed for the dissociation of the $V_{\text{Si}}\text{N}_{\text{C}}$ pair, in which one of the nitrogen atoms moves to a split interstitial $(\text{NC})_{\text{C}}$ site and leaves behind a $V_{\text{C}}V_{\text{Si}}(\text{N}_{\text{C}})_3$ complex leads to an energy increase of 8.9 eV, and requires as much as 9.9 eV. Another way one could imagine for the dissociation of the complex is by a carbon split interstitial $(\text{CC})_{\text{C}}$, which could kick out one of the nitrogen atoms, resulting in a $V_{\text{Si}}(\text{N}_{\text{C}})_3$ and a $(\text{NC})_{\text{C}}$ that could move away in a second step. This process requires ≈ 5 eV, but the resulting structure is 2 eV higher in energy. Obviously, these processes are unlikely to happen at realistic temperatures, and, thus, $V_{\text{Si}}(\text{N}_{\text{C}})_4$ can be expected to survive high temperature annealing.

IV. CONCLUSIONS

In this work, nitrogen in the form of $(\text{NC})_{\text{C}}$ split interstitials is calculated to be mobile at temperatures above 800 °C. Hence, the movement of $(\text{NC})_{\text{C}}$ in bulk material is easier to achieve as diffusion of N ions into SiC, which requires temperatures above 1700 °C. The high mobility of $(\text{NC})_{\text{C}}$ readily explains the annealing of vacancy-related defects between 750 and 1400 °C by defect aggregation with $\text{C}_{\text{Si}}(\text{N}_{\text{C}})_n$ or $V_{\text{Si}}(\text{N}_{\text{C}})_n$ complexes as possible products.

As dissociation of the extremely stable $V_{\text{Si}}(\text{N}_{\text{C}})_n$ complexes is improbable, further aggregation is favored instead, ending up in an electrically and optically inactive $V_{\text{Si}}(\text{N}_{\text{C}})_4$ complex. By its formation four nitrogen dopants are passivated, and, thus this process can explain the as yet unavoidable saturation of free charge carriers above $2 \times 10^{19} \text{ cm}^{-3}$.¹³

Additional creation of $(\text{NC})_{\text{C}}$ split interstitials is only sustained if mobile $(\text{CC})_{\text{C}}$ are available, requiring slightly higher activation energies equivalent to a temperature of about 1000 °C. At these temperatures, a recombination with $V_{\text{Si}}(\text{N}_{\text{C}})_n$ is also possible and, thus, the formation of donors— $\text{C}_{\text{Si}}\text{N}_{\text{C}}$ and $\text{C}_{\text{Si}}(\text{N}_{\text{C}})_2$ complexes—is a competing process. A detailed presentation of our results concerning these defect states of nitrogen in SiC will be given in a forthcoming paper. As a most important result, the $\text{C}_{\text{Si}}\text{N}_{\text{C}}$ pair has a donor level slightly below the conduction band. In order to achieve elevated concentrations of free charge carriers, the annealing circumstances should be optimized for the formation of $\text{C}_{\text{Si}}\text{N}_{\text{C}}$ instead of $V_{\text{Si}}(\text{N}_{\text{C}})_n$. Further experimental and theoretical investigations are necessary to realize this improvement of the annealing process and to achieve higher activation rates of dopant nitrogen.

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