Carbon antisite clusters in SiC: a possible pathway to the D$_{\text{II}}$ center

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The photoluminescence center D$_{\text{II}}$ is a persistent intrinsic defect which is common in all SiC polytypes. Its fingerprints are the characteristic phonon replicas in luminescence spectra. We perform ab-initio calculations of vibrational spectra for various defect complexes and find that carbon antisite clusters exhibit vibrational modes in the frequency range of the D$_{\text{II}}$ spectrum. The clusters possess very high binding energies which guarantee their thermal stability—a known feature of the D$_{\text{II}}$ center. The dicarbon antisite (C$_2$)$_{\text{Si}}$ (two carbon atoms sharing a silicon site) is an important building block of these clusters.

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I. INTRODUCTION

Many unique features of SiC, such as the wide band gap and the very high electrical and thermal stability, render this semiconductor especially important for high power, high frequency and high temperature applications. As for any semiconductor material, the identification and understanding of structural defects and impurities is the key to the technological control of SiC. This is especially important in connection with the ion-implantation, which is inevitably accompanied by the generation of intrinsic defects. Some of these defects are thermally very stable. Two important examples are the photoluminescence (PL) centers D$_1$ (Ref. 1) and D$_{\text{II}}$ (Ref. 2). Although the centers have been extensively studied over the past 30 years their microscopic origin remained unclear. In this work we study carbon antisite clusters and their possible relevance to D$_{\text{II}}$-type centers.

D$_1$ centers are always present in ion-implanted and annealed SiC samples, regardless of the implanted species and the polytype. They were also found (in low concentration) in as-grown material $^4$. The abundance of D$_{\text{II}}$ centers increases significantly at high annealing temperatures (above 1300°C) and the center is thermally stable up to 1700°C. These properties imply that the D$_{\text{II}}$ centers are intrinsic defect complexes. The D$_{\text{II}}$ luminescence originates from the recombination of an exciton bound to the defect. The spectra are usually identified by the main zero-phonon line. The important specific feature of D$_{\text{II}}$ are characteristic phonon replicas above the SiC phonon spectrum. In the original experiments in 3C-SiC the strongest five replicas were highlighted. In later experiments in 4H and 6H-SiC additional localized vibrational modes (LVMs) were observed (more than 12 LVMs have been counted in 4H-SiC $^5$). Many of these observed modes are polytype-independent. A comparison of the spectra from Ref.$^6$ and the earlier Ref.$^2$ reveals that more than the five highlighted LVMs may also be contained in the 3C spectrum. Their spectral density resembles the phonon density of states in diamond, indicating that a carbon-dominated defect is responsible for the observed spectrum.

In this work we consider a number of carbon-related defects in SiC: the carbon di-interstitial, which was the first suggested model for the D$_{\text{II}}$ center, the carbon antisite, the carbon split-interstitials and several carbon clusters. Comparing the calculated LVMs with the experimental D$_{\text{II}}$ spectra we are able to unequivocally rule out all candidates except the carbon antisite clusters. The latter are the only defects that provide a rich LVM spectrum similar to that of the D$_{\text{II}}$ center. The core structure of all these clusters is the dicarbon antisite (C$_2$)$_{\text{Si}}$ (cf. Fig. 1 left) which acts as an aggregation center for further carbon atoms. In this paper we will first present our results for the dicarbon antisite and then consider the formation of more complex defect clusters. We calculate the LVMs associated with these defects and compare them with the D$_{\text{II}}$ spectrum. Although theoretically all these defects can acquire different charge states, we focus on the neutral state as the most relevant for PL. For excitons bound to a charged defect more non-radiative recombination channels are open, and they are unlikely to be seen in PL-experiments $^7$. We also find that the formation kinetics of the carbon clusters agrees with the known features of the D$_{\text{II}}$ center. These results indicate that although neither of the considered defects can alone explain all features of the D$_{\text{II}}$ center, the carbon antisite clusters may serve as a core structure of D$_{\text{II}}$-type defects.

FIG. 1: Structure of the dicarbon antisite (C$_2$)$_{\text{Si}}$ and a carbon cluster with four atoms on a silicon site (C$_4$)$_{\text{Si}}$ in 3C-SiC.
II. METHOD

We employ an ab initio density functional theory (DFT) approach as implemented in the software package FHI96SPIN[20] Smooth norm-conserving pseudopotentials of the Troullier-Martin type[21] and a plane-wave basis-set with a cut-off energy of 30 Ry are used. The exchange-correlation potential is approximated within the LSDA in the parametrization of Perdew and Zunger[22]. In order to reduce the artificial defect-defect interaction, large supercells with 216 lattice sites for 3C-SiC and 128 sites for 4H-SiC are used for all calculations of the defect energetics. For the 216-site cell, the Brillouin zone is sampled by the Γ point, whereas for the hexagonal 128-site cell a special Monkhorst and Pack[23] 2 × 2 × 2 mesh is used. The values of the formation energies are given assuming silicon-rich conditions. Under carbon rich conditions they should be reduced by roughly 3ΔHf = 1.74 eV, where −ΔHf is the heat of formation of SiC. The vibrational properties are calculated using the frozen phonon method. The dynamical matrix

\[ \Phi_{ij} = \frac{1}{\sqrt{m_1 m_2}} \frac{\partial^2 E}{\partial Q_i \partial Q_j} = \frac{1}{\sqrt{m_1 m_2}} \frac{\partial F_i}{\partial Q_j} \]

is calculated by applying displacements \( Q_j \) from the equilibrium configuration and evaluating the force derivatives \( \partial F_i/\partial Q_j \). To obtain noticeable energy changes, the displacements \( Q_j \) ought to be much larger than realistic phonon amplitudes. Therefore it is important to eliminate the anharmonic contribution when evaluating \( \Phi_{ij} \). We do this by applying three different values of the displacement and extracting the linear force constant from a polynomial expansion of the forces. The forces have been converged to a relative accuracy of \( 10^{-4} \). For 3C-SiC, the dynamical matrix is evaluated for a supercell with 64 or 216 sites. The experimental bulk phonon modes are reproduced within 5 percent by this method. Yet the polarization splitting of the TO and LO modes at the Γ point is missing, since the macroscopic polarization of the crystal is incompatible with the periodic boundary conditions imposed on the supercell. We obtain a triple degenerate mode at 115.3 meV, in place of the TO mode of 98.7 meV and the LO mode of 120 meV. For 4H-SiC and for large clusters in 3C-SiC, the computational cost of evaluating the dynamical matrix of the whole 128-site or 216-site supercell is prohibitively large. In these cases we constrain the LVM calculation to the defect molecule (i.e. the dumbbell and its nearest neighbors) embedded in a supercell. We have examined the error resulting from the defect molecule approximation and from the uncertainty in the lattice constant. The results of these tests for a dicarbon antisite in 3C-SiC (see below) are shown in Fig. 2. The lines represent the frequencies of the LVMs versus the defect molecule size calculated at the theoretical (LSDA) lattice constant. The frequencies shift within the grey area when the lattice constant is increased towards the experimental value of 8.239 Bohr. The black bars are the same frequency ranges, but in this case both the electronic structure calculation and the LVM calculation have been performed in a 64 sites cell. We have also verified that under the pressure exerted by the periodic array of defects onto the lattice the lattice constant lies between the indicated limits. The LVM’s variation due to the uncertainty in the lattice constant is thus less than 10 meV. It is also apparent that the defect molecule approximation affects the least localized modes 1 and (to a much lesser extent) 2. The largest effect on the accuracy has the inclusion of the full supercell, which shifts the mode 1 by 14 meV in the 216 sites cell. Compared to the full 64 sites cell, the mode 1 is only 2 meV higher.

III. THE DICARBON ANTISITE

Let us now consider one by one the candidates for the \( \text{D}_{12} \) center as listed above. First, we find that the originally suggested carbon di-interstitial has a formation energy of about 12 eV. This is extremely high even for SiC and practically rules out this model. A similar defect is the carbon split-interstitial \( \text{C}_{sp100} \), i.e. a pair of carbon atoms sharing the same (carbon) site and pointing in (100) direction (in 3C-SiC). This defect also possesses a short carbon-carbon bond and it is energetically the most favorable carbon interstitial. The second lowest carbon interstitial is the carbon-silicon split-interstitial \( \text{C}_{spSi100} \) (a carbon and a silicon atom on a silicon site). Here the additional carbon atom is also connected to its nearest neighbors by short carbon-carbon bonds. However, according to our calculations both defects are very mobile, which is in conflict with the thermal stability of the \( \text{D}_{12} \) center. In addition, we find the LVMs of both defects are not compatible with the \( \text{D}_{12} \)
spectrum. The neutral carbon split-interstitial $C_{\text{sp}}^{\langle 100 \rangle}$ in the tilted structure has two LVMs at 120.4 and 188.7 meV and LVMs in the phonon gap. The carbon-silicon split-interstitial $C_{\text{spSi}}^{2+}$ possesses a richer vibrational spectrum but still with only three non-degenerate LVMs above the bulk spectrum. This also does not match the number of the characteristic $D_{11}$ lines. Another possible candidate could be the carbon antisite $C_{\text{Si}}$. Following the carbon vacancy $V_C$ it is the second most abundant defect in SiC. However, it shows only vibrational resonances in the bulk phonon spectrum and has no true LVMs. Also small clusters of carbon interstitials do not provide LVMs compatible with the $D_{11}$ spectrum.

The simplest candidate that possesses the main features of the $D_{11}$ center is the dicarbon antisite $(C_2)_{\text{Si}}$ that we have already mentioned above in connection with Fig. 2. The dumbbell of two carbon atoms sharing a silicon site (highlighted atoms in Fig. 2 left) is surrounded by a tetrahedron of four carbon atoms. In 3C-SiC the dumbbell is pointing in $(100)$ direction whereas in 4H-SiC it is oriented either along the $(10 \bar{1} 1)$ or the $(1 \bar{1} 0 1)$ direction. Depending on the Fermi level, the defect may acquire the charge states from $2^+$ through $2^-$. We find that the dicarbon antisite has a relatively low formation energy. For the neutral charge state the values are 6.7 eV and 7.8 eV in 3C and 4H polytypes, respectively. In 4H-SiC two possible substitutional configurations exist, i.e., hexagonal ($h$) and cubic ($k$), but the formation energy at these two sites only differs by 0.1 eV. These values are comparable to the formation energies of $C_{\text{sp}}^{\langle 100 \rangle}$ and $C_{\text{spSi}}^{\langle 100 \rangle}$. Still, the calculated formation energy indicates that its equilibrium abundance is too low for experimental observation. Hence kinetic effects should play an important role in the dicarbon antisite formation. On the other hand, once created, the defect has a very high stability, as reflected by the high binding energy. Before we turn to kinetic aspects, we discuss the electronic properties and the LVMs of the dicarbon antisite.

In 3C-SiC, the dicarbon antisite possesses two degenerate defect orbitals with energy levels in the band gap. In the neutral charge state these orbitals are occupied by two electrons, which can form either a spin 0 (low-spin) or a spin 1 (high-spin) configuration. According to the calculation, the high-spin state is about 80 meV lower in energy than the low-spin state. This energy difference is, however, too small to uniquely determine the ground state spin configuration. For this reason we consider both options. The defect wave function consists of bonds between the three upper carbon atoms and the three lower carbon atoms of the defect tetrahedron (cf. Fig. 2 left). In the low-spin configuration, one of these bonds is fully occupied, resulting in a splitting of the defect levels and a Jahn-Teller distortion, with the upper or the lower pair of the tetrahedron being stretched. This reduces the original $D_{2d}$ symmetry to $C_{2v}$. In the high-spin configuration, both bonds are equally occupied, retaining the degeneracy and the $D_{2d}$ symmetry. As we discuss below, this geometrical difference is reflected in the vibrational modes of the defect. In 4H-SiC, the high-spin state is about 120 meV lower than the low-spin state, which is—as in 3C-SiC—a very small energy difference. Due to the lower symmetry of the crystal, the symmetry group is always $C_{1h}$. The defect’s structure on the cubic and the hexagonal site is qualitatively similar.

As outlined above, the dicarbon antisite is the simplest defect that possesses LVMs that are similar to the phonon spectrum of the $D_{11}$ center. The calculated frequencies (using a 64-sites supercell) for the neutral charge state in low-spin and high-spin configurations are listed in Tab. I along with the experimental data for the five characteristic $D_{11}$ phonon modes and our calculated results for the two neighboring dicarbon antisites. We see that in the 3C polytype the low-spin configuration provides an LVM pattern similar to the five phonon replicas of $D_{11}$. Similar results are obtained for 4H-SiC, except that the frequencies of the modes 1 to 4 are lowered due to the defect molecule approximation.

In spite of a different crystal symmetry, the vibrational patterns of the LVMs in 3C- and 4H-SiC are very similar, owing to the localized nature of the vibrational modes. The highest mode 5 is a stretching vibration, where the two atoms of the dumbbell oscillate against each other. Its calculated frequency is about 8% higher than the experimental value. However, this is the usual accuracy of these defect calculations. The modes 3 and 4 represent an oscillation of one of the dumbbell atoms against its neighbors. In 3C-SiC, these modes are affected by the Jahn-Teller distortion of the low-spin configuration. As expected from the symmetry, the modes are degenerate in the high-spin and non-degenerate in the low-spin case. This effect can also be seen in Fig. 2 where the 216 sites calculation, although performed spin-unpolarized, has been performed in a high-spin like configuration. Considering the small energy difference between the high-spin and the low-spin configuration both options should be allowed. In addition to the already mentioned clustering of carbon atoms, this may be a source of further lines in the luminescence spectra. In 4H-SiC, the modes 3 and 4 are always non-degenerate, although the splitting in the high-spin configuration is smaller than in the low-spin configuration, due to the lower symmetry of the crystal field. The mode 2 describes the vibration of the dumbbell along its axis against the enclosing tetrahedron. The mode 1 is the least localized mode and therefore it is most affected by the employed supercell technique. This mode corresponds to a breathing-like vibration of the enclosing tetrahedron. While for the low-spin case the breathing mode lies above the highest bulk vibration, it is in resonance with the bulk spectrum and lies 8 meV below the calculated value of the highest bulk mode for the high-spin case in a 64 sites cell. This is in agreement with Gali et al. (Ref. 18) who considered the high-spin state of $(C_2)_{\text{Si}}$. In 4H-SiC, a similar behavior is not obvious from our results, as the effect may be masked by the defect molecule approximation. In addition to the high-
modes 3 and 4 are degenerate in the charge states 2 due to the occupation of the bonds. For 3C-SiC, the trons, resulting from an expansion of the defect molecule frequencies with the increase of the number of localized electrons, resulting from an expansion of the defect molecule due to the occupation of the bonds. For 3C-SiC, the modes 3 and 4 are degenerate in the charge states 2+ and 2−, since the electronic defect levels are either empty or fully occupied, and a Jahn-Teller distortion is suppressed.

IV. CLUSTERING OF CARBON ATOMS

Usually, the D11 center is observed in ion-implanted and annealed samples. It is stable up to temperatures of 1700°C. This and the previously discussed low equilibrium concentration suggest a kinetically controlled formation of this defect from non-equilibrium vacancies and interstitials. At first, a carbon antisite is formed via a recombination of a carbon interstitial with a silicon vacancy. It merges then with a mobile carbon split-interstitial. At first, a carbon antisite is formed via a recombination of a carbon interstitial with a silicon vacancy. It merges then with a mobile carbon split-interstitial.

Adding a further carbon atom to the dicarbon antisite by aggregating carbon split-interstitials around the core. In addition to the clusters located around a single silicon site, aggregates of several dicarbon antisites are also possible. A pair of the dicarbon antisites in 3C-SiC ((C2)Si)2 is shown in Fig. 3. In 4H-SiC three different configurations, which can be compared to its 3C-SiC counterpart, are possible when the two di-antisites occupy two cubic (kk), two hexagonal (hh) or cubic-hexagonal (kh) sites. As an exemplary structure we have considered in detail the kh-configuration, which has a local geometry similar to the 3C-SiC case (Fig. 3), but the bond length between the neighboring dicarbon antisites is shorter. We found that this defect is very stable in both polytypes: in 3C-SiC it costs about 5.9 eV to remove a carbon atom, whereas in 4H-SiC this energy is 6.7 eV. The calculated LVMs of both complexes are given in Tab. II. They have been calculated using the defect molecule approximation that allows the vibration of the two dumbbells and of the surrounding carbon neighbors within the 216 (3C-SiC) and 128 (4H-SiC) sites cell. As discussed above, the numerical results are affected by the defect molecule approximation. Alternatively, one could work with the smaller 64 sites cell which would allow to calculate the dynamical matrix of the whole cell. However, we find that in this cell the electronic structure is so strongly distorted by the proximity effects that it is unacceptable for the analysis of the LVMs. For the pair of dicarbon antisites the highest almost degenerate modes 5 and 6 involve a stretching vibration of the dumbbells, similar to the lone dicarbon antisite. Due to the interaction of the dumbbells these modes become softer and combine into anti-symmetric and symmetric vibra-

| LVM | 3C | 4H |
|-----|----|----|
|     | (C2)Si, ls | (C2)Si, hs | (C2)Si, exp. |
| 1   | 116.4 | 107.6 | 123.3 | 127.8 |
| 2   | 128.5 | 123.2 | 125.6 | 130.9 |
| 3   | 139.4 | 141.7 | 127.1 | 146.3 |
| 4   | 148.3 | 141.8 | 139.3 | 152.2 |
| 5   | 177.5 | 177.5 | 168.6 | 164.7 |
| 6   |       |       | 169.7 |
tions. The modes 3 and 4 represent a motion of the two lower and upper carbon atoms of the dumbbells in bond direction against their surrounding neighbors, respectively. In 4H-SiC, the defect shows a similar behavior, but the energy of all modes is by about 8 meV lower than in 3C-SiC so that the lowest mode (with an energy of 114.4 meV) drops into the bulk phonon spectrum. This effect and also the larger frequency difference between the stretching modes reflects the stronger relaxation of the defect in this polytype. We have recently learned that A. Gali et al. calculated the LVMs of the kk-configuration, finding results similar to the 3C-SiC values, and speculated that this defect was the D\textsubscript{11} center. As the kk-configuration has a 3C-like environment (in contrast to the kh-configuration), the similarity to 3C-SiC is quite natural. However, the conjecture that the ((C\textsubscript{2})(Si))\textsubscript{2} model completely describes the D\textsubscript{11} center does not seem to be supported by experimental data. Recent experiments have investigated the multitude of zero phonon lines (ZPLs) as well as the phonon replicas\textsuperscript{6} of the D\textsubscript{11} center. In 6H-SiC, Sridhara et al.\textsuperscript{6} concluded from temperature and stress-dependence experiments that the four ZPLs of D\textsubscript{11} stem from the different excitonic states of the bound exciton (one ground state and three excited states), but not from different binding centers of the same exciton. Regarding the phonon replicas in 4H-SiC more than 12 LVMs and a single ZPL have been reported by Carlsson et al.\textsuperscript{5} which is consistent with the earlier results for 4H and 6H-SiC of Sridhara et al.\textsuperscript{6} In addition, as we noted above, a comparison of the spectra in 3C, 4H and 6H-SiC\textsuperscript{6} indicates that more than five LVMs may be present also in 3C-SiC. The apparent large number of phonon replicas in 4H and 6H-SiC makes it tempting to assume that they originate from different geometrical configurations of the same simple defect. For example, for the ((C\textsubscript{2})(Si))\textsubscript{2} in 4H-SiC this would be kk, hh and kh. This assumption has, however, the following implications. Firstly, it follows that a larger number of LVMs should be present in 6H-SiC than in 4H or 3C-SiC, since less or no inequivalent sites are available in the two latter polytypes. Secondly, the different configurations should give rise to a multitude of exciton ground-state ZPLs. According to the conclusion of Sridhara et al.\textsuperscript{6} and the rich vibrational structure contained in all polytypes (cf. discussion above) this is not evident from the experiments. This applies, in particular, to the ((C\textsubscript{2})(Si))\textsubscript{2} defect. Furthermore, the LVM pattern of this defect is, in fact, not compatible with the D\textsubscript{11} spectrum. The small splitting of the two highest LVMs (see Tab. 1), which persists through different polytypes and configurational models, is not observed in the D\textsubscript{11} spectrum which has nearly equidistant lines. Thus the ((C\textsubscript{2})(Si))\textsubscript{2} model alone cannot explain all features of the D\textsubscript{11} center. Larger carbon clusters are likely to be involved. For such clusters the differences between the polytypes lose their importance. This may be responsible for the polytype-independent LVMs of the D\textsubscript{11} centers. Further experimental data are necessary to clarify the situation, especially for the 3C polytype, which lacks inequivalent lattice sites.

V. CONCLUSION

In conclusion, we have analyzed the structural, electronic and vibrational properties of the dicarbon antisite complex. The defect possesses a characteristic vibrational pattern in the frequency range of the D\textsubscript{11} spectrum, but cannot explain all the phonon replicas observed. Yet, we find that the dicarbon antisite can act as an aggregation center for carbon clusters that allow for a much richer phonon spectrum. All the defect complexes presented above possess very high dissociation energies, which guarantee their high thermal stability. Due to the high formation energies, these defects can exist in as-grown material only in very low concentrations but can be kinetically created during the annealing. Yet, none of the considered defect complexes can explain all features of the D\textsubscript{11} center. Most probably the D\textsubscript{11}-type centers are related to larger carbon clusters with the dicarbon antisite playing the role of an elementary building block of the aggregates.

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