

Electrical characterization of metastable carbon clusters in SiC: A theoretical study

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First-principles calculations carried out in 3C- and 4H-SiC show that small metastable carbon clusters can be created in irradiated SiC. The metastable carbon clusters possess occupation levels in the p -type as well as in the n -type 4H-SiC. Depending on the conditions of irradiation and the annealing temperature new photoluminescence centers might be detected with characteristic local vibrational modes in the spectrum. We provide the occupation levels and the local vibrational modes of the defects to make the identification possible.

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Interstitial clusters can form in irradiated semiconductors, and those can strongly influence the activation of implanted dopants. Evidence of intrinsic related metastable defects in n -type SiC has been already shown by deep level transient spectroscopy (DLTS) measurements.^{1,2} There have also been reports on persistent photoconductivity (PPC) in 6H-SiC (Refs. 3–6) indicating the existence of defects with metastable states. Unfortunately, these DLTS and optical admittance spectroscopy (OAS) centers were rarely correlated to other properties of the defects making the identification rather difficult.

In earlier studies it was shown that carbon interstitial and carbon antisite defects were created in irradiated SiC, those could be stable against very high temperature (>1000 °C) annealing.^{7,8} The local vibrational modes of these defects in the neutral charge state were already given.^{7,8} These carbon clusters are the aggregates of the mobile^{9,10} carbon self-interstitials. The neutral isolated carbon split-interstitial (C_i) itself has two metastable states at the k -site in 4H-SiC. The most stable form is a tilted structure with $S=0$ state (see Ref. 11). Our calculated local vibrational modes (LVMs) are at 1507 cm^{-1} (187 meV) and at 944 cm^{-1} (117 meV). At an appropriate temperature it can transform to another configuration with $S=0$ state (shown in Fig. 5a in Ref. 7). There is only one LVM above phonon continuum in this case at 1477 cm^{-1} (183 meV) while the most symmetric configuration with $S=1$ state possesses a 100 cm^{-1} higher LVM at 197 meV.⁷ At h -site it has a symmetric configuration. The accumulation of two C_i 's results in basically three different structures possessing different local vibrational modes.⁷ These are in the order of their stability: the pentagon structure, the ring structure and the ladder structure.⁷ The stability of these defects have been established by calculating the binding energy (E_b) of them,

$$C_i + C_i \xrightarrow{-E_b} (C_i)_2, \quad (1)$$

where $(C_i)_2$ is the actual configuration of two C_i 's. If the binding energy was positive then it means that the complex formation is favorable. We shall use this definition for the binding energy of other aggregates as well in this paper.

Beside the carbon interstitials the carbon antisite can play a crucial role in forming carbon aggregates in SiC since C_{Si} has the lowest formation energy among the intrinsic defects in a wide range of Fermi level. It has been already shown that C_{Si} can also accumulate carbon interstitials.^{7,8} C_{Si} with the captured C_i are sharing the silicon site ($(C_2)_{Si}$), called to be the dumb-bell configuration¹² or split-interstitial configuration.⁸ We associated the $(C_2)_{Si}$ defect with the P -T photoluminescence (PL) centers detected in electron irradiated 6H-SiC based on the calculated stability and LVMs.^{7,12} The thermally stable $(C_2)_{Si}$ defect can be approached by an additional mobile C_i . The most stable configuration is a triangle of three carbon atoms sharing one vacant silicon site ($(C_3)_{Si}$) found by Mattausch and co-workers.⁸ Our calculated binding energy is 5.1 eV and our calculated highest LVMs are 2088, 1493, 1291, 1094, 1075 cm^{-1} , respectively. This defect is responsible for the U PL line in electron irradiated 6H-SiC.^{8,12} We have found earlier a metastable ring structure with a binding energy of 4.2 eV in 4H-SiC which has lower LVMs.⁷

The earlier theoretical studies on carbon aggregates were focused mainly on finding the most stable complexes and on providing the local vibrational modes for the *neutral* defects. In this paper we will provide a detailed electronic structure of the electrically active *metastable* carbon clusters by means of first principle calculations. We will show that some DLTS or admittance spectroscopy (AS) centers may be associated with these metastable carbon clusters. We give here configurations for the $(C_i)_2$ defect in 4H-SiC which have not yet reported earlier. We have found metastable carbon clusters with low local vibrational modes which may be detected in the photoluminescence spectrum. We will give the calculated local vibrational modes to help in identification of these defects.

Ab initio calculations based on density functional theory in the local density approximation¹³ (LDA) with the exchange correlation of Ceperley-Alder¹⁴ were carried out in the framework of the SIESTA code.¹⁵ A 64 atom cubic supercell of 3C-SiC and a 96 atom hcp supercell of 4H-SiC with 8 K -points were used with a numeric atomical orbital basis set (double ζ polarized with 0.02 Ry energy shift) and

norm-conserving Troullier-Martins pseudopotentials¹⁶ to determine the equilibrium configurations, relative stabilities and occupancy levels of the defects. This method can provide similar results compared to those obtained by well converged plane wave supercell calculations even for vacancies.⁷ The total energy is minimized as a function of the coordinates until the forces were below 0.04 eV/Å. The local vibrational modes have been calculated in the quasiharmonic approximation using the first numeric derivative of the forces. The error bar of LVMs are typical within 30 cm⁻¹ for the stretch modes. Therefore, LVMs close or within the top of the phonon continuum are given. All the atoms in the defective supercells were allowed to relax and to vibrate. Since the calculation of LVMs is an extremely demanding process, the LVMs were determined for the significantly different structures in 3C-SiC (the minor difference between the *h* and the *k* sites in 4H-SiC was not considered). The so-called “gap” problem of the LDA method has been circumvented by another method using the CRYSTAL2003 code¹⁷ with a modified BLYP functional in which the experimental width of the gap of 3C- and 4H-SiC could be reproduced (see Ref. 7 for more details). Using the same defective supercell and *K*-point set the position of the defect levels in the band gap have been calculated by the modified BLYP functional. This methodology gives practically identical one-electron levels for interstitial defects in SiC as an approximate GW correction to the LDA.¹⁸ The calculated occupied one-electron LDA Kohn-Sham defect levels in the SIESTA code were *a posteriori* shifted into the position of the modified BLYP’s values. The total energy of the defects in the SIESTA code was also corrected accordingly. The total energy of the charged supercell has been corrected according to the results of Ref. 19. By using these corrections the (*q*1/*q*2) occupation level of the defects has been determined where *q*1 and *q*2 are the possible charge states of a given defect. This gives the position of the Fermi level where the formation energies of a given defect in these *q*1/*q*2 charge states are equal.

First, we considered the isolated carbon interstitial in 4H-SiC. This defect behaves differently on the two sites in 4H-SiC. At *h*-site *C_i* has symmetric dumb-bell configuration in the charged states of (2+) up to (−) but it transforms to a tilted configuration in the (2−) charged state. Due to the reconstruction, it is a negative-*U* center possessing the (0/2−) level at $E_V+2.5$ eV, where E_V is the top of the valence band. This agrees with the measured E_i level at $E_V+2.5$ eV in electron irradiated 6H-SiC (Ref. 20) which anneals out at low temperature. Doyle and co-workers have also found acceptor levels at $E_V+2.62$ eV and $E_V+2.98$ eV in electron irradiated 4H-SiC which anneal out at low temperature simultaneously. They may correspond to the calculated (0/2−) level of *C_i-h* ($E_V+2.5$ eV) and the (−/2−) level of *C_i-k* ($E_V+3.1$ eV). The (0/−) level of *C_i-k* is at $E_V+2.0$ which should be detected by DLTS or AS annealing out at low temperature simultaneously with the others. The calculated (2+/+) and (+/0) levels are close to the midgap at around $E_V+1.3$ – 1.4 eV for both *k* and *h* sites which should correlate to the acceptor levels of this defect.

The combination of two carbon interstitials can result in the pentagon structure with a binding energy of 3.0 eV.⁷ The

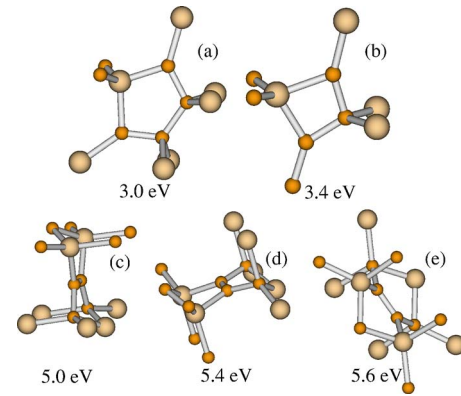


FIG. 1. (Color online) Stable and metastable (C_i)₂ defects in 4H-SiC. The calculated binding energies are shown below the figures of the defects. (a) Pentagon structure, (b) ring structure, (c) ladder structure parallel to *c* axis, (d) ladder structure in the hexagon, (e) ladder structure in between *k* and *h* sites.

binding energy of the pentagon structure indicates that this defect is stable unless it transforms to a more favorable configuration. The annealing temperature of this defect then depends mainly on the energy barrier of this transformation. The pentagon structure [Fig. 1(a)] can be transformed easily to the most stable ladder structure [Fig. 1(e)] just by rotating the two carbon interstitial atoms out of the (1120) plane breaking one Si-C bond while making a new Si-C bond and a double C-C bond. That means that the pentagon structure can transform to the most stable configuration at relatively low temperature annealing. The pentagon structure has one fully occupied and one empty level in the gap. The defect states are due to the interacting *p* orbitals of the two *C_i*’s in the defect pointing out of the plane of the pentagon. The (2+/+) occupation level of the pentagon structure is at $E_V+1.6$ eV. The (+/0) and (0/−) levels are very close to each other at around $E_V+1.7$ eV. In the negatively charged state the carbon interstitials start to move out the plane of the pentagon and the double negatively charged state is no longer stable. The aforementioned occupation levels might be detected by AS annealing out at low temperature.

The second stable configuration is the ring structure.⁷ In the ring structure the two *C_i*’s are closer to each other sharing the first neighbor C atom, that can either be at the *k* site or at *h* site in 4H-SiC [see Fig. 1(b)]. The difference in the geometry and in the corresponding total energy at the *k* and the *h* sites is minor. The ring structure consists of short C-C bonds with *sp*² and *sp*³ configurations as well. In 4H-SiC the defect possesses three levels in the gap. Two defect levels are fully occupied lying at $E_V+0.4$ eV and $+1.7$ eV. The first one is due to the bond between one of the *C_i* and its first neighbor C atom and the wave function is partly localized on the Si atom constituting the ring as well. The second occupied defect level is mostly localized on the *p* orbital of the two *C_i*’s pointing out of the plane of the ring. The third defect level is again strongly localized on the two *C_i*’s *p* orbital. The ring structure can be theoretically in the (3+) and (4+) charged states but the corresponding occupation levels are falling to the valence band. The defect, however, possesses two donor occupation levels at $E_V+1.2$ and $+2.0$ eV, and an acceptor

level at $E_V+2.7$ eV. Doyle and co-workers have found two acceptor levels at around $E_V+2.7$ eV with a simultaneous disappearance of DLTS levels at $E_V+2.62$ eV and $E_V+2.98$ eV at low temperature annealing. We attribute the last two DLTS levels to the mobile C_i 's which can form the metastable ring structure giving rise to an acceptor level at $E_V+2.7$ eV.

In the most stable structure (called ladder) the two C_i 's are situated at the puckered bond center site bending to each other.⁷ This can happen either in the plane of the ladder parallel to the c axis [Fig. 1(c)] at both k or h sites, or not parallel to the c axis [Fig. 1(d)] at both k or h sites, or the ladder makes a bridge between the h and the k sites [Fig. 1(e)]. The difference between the h and k sites for the first two ladder structures is minor therefore the configurations at the k sites are considered. We have found that the binding energy difference is significant between these configurations and the bridge-ladder configurations is the most favorable complex with a binding energy of 5.6 eV. Interestingly, all these ladder structures have similar electronic structure: they possess one defect level at around $E_V+0.3$ eV due to the sp^2 orbitals of C_i 's. The different binding energy is due to the difference in the relaxations. The ladder structure is a very effective hole trap: the $(2+/+)$ and $(+/0)$ levels are at around $E_V+0.35$ eV. Since the binding energy of the most stable ladder structure is extremely high (~ 5.6 eV), it should be stable after very high temperature annealing. A new DLTS center (KR1) has been found recently which appears in H^+ , He^+ implanted p -type $6H$ -SiC. The concentration of KR1 center increases with the annealing temperature up to the highest temperature of 1700 °C that could be studied in the experiment.²¹ We believe that this very high thermal stability can be associated with the ladder structure of $(C_i)_2$. We considered then the complex of one or two carbon interstitials with a carbon antisite defect. The defect of one C_i and C_{Si} results in $(C_2)_{Si}$ as described in the introduction. The neutral defect can have very complicated excitation schemes as it is explained in Ref. 7: the defect possesses nearly double degenerate levels in the midgap in $4H$ -SiC due to the p orbitals of the two carbon atoms in the core of the defect occupied by two electrons. We found that the asymmetric $S=0$ state is about 0.2 eV higher in energy than that of the symmetric $S=1$ state in $4H$ -SiC. This means that metastable forms of the P - T centers¹² might be detected in the PL spectrum. The nearly double degenerate defect levels can be doubly positively and/or negatively ionized. In the double negatively charged state a tilted configuration occurs which raises the total energy of the defect. As a consequence, the $(2-/-)$ level is at $E_V+2.9$ eV while the $(0-/-)$ level lies much lower at $E_V+1.9$ eV. These levels beside the donor levels at about $E_V+1.3$ eV might be correlated with the P - T PL centers in $6H$ -SiC.¹² The $(C_2)_{Si}$ defect can be approached by an additional C_i resulting in $(C_2)_{Si}-C_i$ defects in irradiated SiC. We report here two new metastable structures. Depending on the actual motion of C_i two pentagon structures can be formed with binding energies of 0.6 and 1.4 eV, respectively [see Figs. 2(a) and 2(b)]. The first one is only slightly stable and could be of marginal interest. For the sake of completeness we provide the local vibrational modes for both defects in

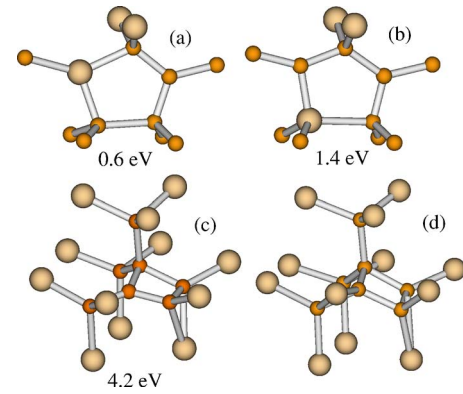


FIG. 2. (Color online) Metastable $(C_2)_{Si}-C_i$ defects in SiC. The calculated binding energies for the neutral defects are shown below the figures of the defects. The double negatively charged ring structure is also shown to explain the negative- U property. (a) Pentagon-1 structure, (b) pentagon-2 structure, (c) the neutral ring structure, (d) the double negatively charged ring structure.

Table I. They possess relative low LVMs due to the weak C-C bonds. The pentagon structures have defect levels in the midgap. At relatively low temperature annealing the metastable $(C_2)_{Si}-C_i$ defects may form which can then either dissociate into isolated mobile C_i and immobile $(C_2)_{Si}$ or transform to the stable triangle⁸ or ring⁷ structures. This means that new PL lines might be associated with the pentagon structures possessing low LVMs (see Table I) at low temperature annealing while at higher annealing temperatures new PL centers would arise with higher LVMs in the phonon assisted sidebands of the spectrum. The most stable triangle structure was found by Mattausch and co-workers:⁸ the three carbon atoms share one vacant Si-site forming a triangle structure with very short C-C bonds [$(C_3)_{Si}$ defect]. It has a defect level at about $E_V+0.4$ eV; it is a very effective hole trap. The $(2+/+)$ level is very close to the valence band maximum while the $(+/0)$ is around $E_V+0.4$ eV. This defect could be responsible for thermally very stable and immobile DLTS or minority carrier trap centers in irradiated SiC (Refs. 21 and 22) which may correlate with the U PL center.¹²

The ring structure is also a very stable defect with a binding energy of 4.2 eV possessing one occupied and one empty defect level in the gap. These defect levels arise from the p orbitals of the interstitial carbon atoms. The defect possesses

TABLE I. Local vibrational modes of the three isomers of $[(C_2)_{Si}-C_i]$ defect. The order of the isomers is as depicted in Fig. 2. The local vibrational modes are given in cm^{-1} and in meV as well. The meV values are in parentheses.

Pentagon-1	Pentagon-2	Ring
1272 (158)	1274 (158)	1529 (190)
1206 (150)	1155 (143)	1486 (184)
1087 (135)	1133 (140)	1231 (153)
994 (123)	1043 (129)	1110 (138)
943 (117)	962 (119)	1103 (137)
	957 (119)	

($2+/+$) and ($+/0$) levels at about $E_V+0.9$ and $+1.1$ eV, respectively. The ring structure has acceptor levels as well. The defect changes its configuration considerably transforming one sp^2 C atom into an sp^3 one [see Figs. 2(c) and 2(d)] if the defect was negatively ionized. It shows a significant negative- U behavior: the calculated ($0/2-$) level is at about $E_V+2.7$ eV. This is close to the thermally stable $Z1/Z2$ DLTS levels in $4H$ -SiC.^{23,24} The relatively high binding energy of this intrinsic defect (4.2 eV) might support the model as a candidate for $Z1/Z2$ DLTS center. This model can explain the intrinsic nature of the $Z1/Z2$ center²⁵ and why this center forms far from the irradiation region in SiC.²⁶ It has been recently found²⁶ that the concentration of $Z1/Z2$ DLTS center reduced after high temperature annealing but still persisted up to 2000 °C. This would indicate a high stability which cannot be explained by the binding energy of the model. However, the ladder (C_i)₂ defect [beside the triangle (C_3)_{Si} defect] should exist and dissolve at this temperature²⁷ due to its extremely high binding energy. This could continuously emit additional mobile C_i 's attached to the immobile C_{Si} to create the $Z1/Z2$ defect explaining their existence after such a high temperature annealing. This scenario might be proven by monitoring the DLTS or minority carrier trap centers at around $E_V+0.35$ eV at this annealing temperature.

It is desirable to investigate the possible correlation between the $Z1/Z2$ DLTS center with carbon-related PL centers possessing high LVMS at around 1500 cm^{-1} (see Table I) in order to identify the $Z1/Z2$ center.

In summary, based on first principles calculation we have shown that carbon interstitials can form electrically active metastable defects. These electrically active metastable carbon clusters are annealed at different annealing temperatures depending on their dissociation energy. We provide the occupation levels and local vibrational modes of these defects as spectroscopic fingerprints. Since some defects have donor and acceptor levels as well we suggest to make OAS or DLTS experiments in p -type and n -type irradiated SiC with the same irradiation condition in order to correlate deep donor and acceptor levels of the same defect. In the PL spectrum new carbon related centers are expected to appear at low temperature annealing due to pentagon structures with highest LVMS at around 158 meV. We propose a model for the well-known $Z1/Z2$ DLTS center in $4H$ -SiC.

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