

Overcoordinated Hydrogens in the Carbon Vacancy: Donor Centers of SiC

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Epitaxial silicon carbide is likely to contain hydrogen and vacancies (V); therefore, $V + nH$ complexes are likely to influence its electronic properties. Using *ab initio* calculations we show that neutral and positive H atoms are trapped by carbon vacancies (V_C) in *three-center bonds* with two Si neighbors. The double positive charge state of $V_C + H$ is not stable in equilibrium and in the triply positive state H binds only to one of the Si neighbors. At most two H atoms can be accommodated by a single V_C . The $V_C + nH$ complexes have donor character and exhibit rather atypical vibration modes for Si-H bonds. Occupation levels and spin distributions were calculated and compared for $V_C + H$ and V_C .

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Over(under)coordination usually causes electrically active defect states in electronic materials. Undercoordination of silicon [1] as well as overcoordination of oxygen [2,3] is well known to produce gap states in the Si/SiO₂ system. Among the impurities, hydrogen is probably the least expected to be overcoordinated but, as an isolated neutral or positive interstitial in silicon (or diamond) [4–8], it inserts itself between two bonded Si (C) neighbors forming a *three-center bond* (three atoms sharing a pair of electrons, the orbital of which envelops all three of them). In other semiconductors, however, the hydrogen interstitial is predicted to reside mostly at a so-called antibonding position—making the nearest host atom overcoordinated [9,10]. This is also the case for silicon carbide (SiC) [11]. The development of SiC as device material for high temperature, high power, and radiation resistant applications is making continuing progress. Hydrogen is incorporated into SiC during epitaxial growth but little is known about its effects. Experimental studies devoted to the identification of H-related defects are scarce. Vibrations close to 3000 cm⁻¹ have been observed and assigned to C-H bonds but no bands typical of Si-H bands around 2100 cm⁻¹ have been seen [12]. Theoretically only interstitial H was investigated in SiC [11]. Vacancies are present in epitaxial SiC, are created also by irradiation, and may serve as traps for interstitial H.

In this paper we show that in SiC—grown in hydrogen ambient (especially at high Si/C ratio)—electrically active, bistable, negative- U complexes of carbon vacancies (V_C) and hydrogen may exist. (However, if silicon vacancies are present in high concentration then the diffusing hydrogen is preferentially trapped by them. The results of our studies on $V_{Si} + nH$ complexes and interstitial hydrogens will be published elsewhere [13].) V_C can also trap two hydrogens (but no more). The $V_C + 2H$ com-

plex gives rise to a double donor level. Therefore, unlike in other semiconductors this vacancy cannot be passivated by hydrogens. The $V_C + nH$ complexes exhibit peculiar Si-H related local vibration modes (LVM).

The calculations are based on density-functional theory in the local-density approximation (LDA) [14]. The FHI96MD code [15] was used for plane-wave supercell (SC) calculations with a 64 Ry energy cutoff. In this case Troullier-Martins pseudopotentials [16] were used to describe the core of the atoms. A bcc supercell consisting of 32 atoms was employed to model cubic silicon carbide with Brillouin-zone sampling on the $2 \times 2 \times 2$ Monkhorst-Pack mesh [17]. The defect geometry was determined by allowing two shells of host atoms to relax around the defect. The convergence criteria for the forces was 0.0005 hartree/bohr. Relative stabilities and occupation levels have been determined by correcting for the LDA gap error [18]. Tests carried out in 128-atom supercell calculations showed only a difference of <0.05 eV in the relative stabilities. LVMs and spin distribution can more easily be calculated using a localized basis set. For that purpose spin polarized LDA using the AIMPRO [19] code was applied with a high quality basis: 8-8 independent s and p Gaussians for Si and C, 3-3 s and p for H, as well as 3 s -type Gaussians in bond centers between atoms of the first two neighbor shells around the defect. These shells were allowed to relax to find the defect geometry with minimum energy. In the calculation of LVMs the forces were determined for all the relaxing atoms. The calculated LVMs are accurate within about 40 cm⁻¹. Mulliken analysis was carried out by projecting the wave functions onto a contracted minimal basis set. Bachelet-Hamann-Schlüter [20] pseudopotentials were used to describe the core of the atoms in the AIMPRO calculations, and cubic (3C) SiC was modeled by a hydrogen terminated, carbon-site centered

$C_{29}Si_{42}H_{60}$ molecular cluster (MCM) with T_d symmetry. Control calculations on a $C_{28}Si_{33}H_{56}$ MCM, modeling the hexagonal $4H$ polytype at the k site (C_{3v} symmetry), have also been carried out.

In the SC calculations the lattice constant was optimized for the perfect supercell and found to be within 0.8% of the experimental value. The relaxed geometry and formation energy of V_C in this SC was checked against the results of Ref. [21], obtained in a 216 atom SC calculation using four special K points. Our calculation resulted in a formation energy (relative to the binding energy per atom in the stoichiometric compound) of $E_f = 6.54$ eV at 2.6% inward breathing and 7.7% pairing distortion [22] of the vacancy neighbors, to be compared to the values of 6.22 eV, 2.8%, and 10.6%, respectively, obtained in Ref. [21]. Based on the latter calculation a stoichiometry- and doping-independent energy of 4.30 eV was given for the neutral V_C in Ref. [23]. Our corresponding value is 4.45 eV. This shows that our calculation indeed gives geometry and total energy near to convergent values. The dispersion of defect bands was less than 0.5 eV. Position of isolated defect levels were obtained by a tight-binding fit. In the perfect MCM, the host atoms were placed at ideal lattice positions and the length of the terminating Si-H and C-H bonds have been adjusted to give the most homogeneous charge distribution for both sublattices and no hydrogen levels around the "gap" of the perfect cluster. The difference in the absolute values of the Mulliken charge is within $\pm 0.1e$ for all relaxing Si and C atoms. For all the defects studied here, the optimum geometries obtained from the MCM calculations were practically identical with those found in the SC calculations.

Intuitively, one expects a single H to saturate one dangling bond of a vacancy and, with two others rebonding, to leave one singly occupied dangling bond (C_{1h} symmetry, as is the case for a $V + H$ complex in Si). This structure turns out to be metastable in SiC (both $3C$ and $4H$ SiC). Hydrogen in a symmetric position between two Si atoms, forming a three-center bond (see Fig. 1), is more stable by 0.5 eV (all energy values quoted refer to $3C$). The symmetry of this $V_C + H$ complex is C_{2v} in $3C$ SiC (C_{1h} in $4H$). Overcoordination is quite unique for a hydrogen trapped by a vacancy in a semiconductor. The reason is that the Si-Si distance across the carbon vacancy in SiC is about 3.1 Å while the normal Si-H bond length is ~ 1.5 Å, so the H atom can interact with at least two Si atoms. The resulting electronic structure is very similar to that of the bond-center H interstitial in silicon and diamond. Mulliken analysis shows that the two-center long bond between two Si neighbors of the reconstructed carbon vacancy becomes a three-center bond, enveloping the H atom between the two Si atoms. The one-electron level corresponding roughly to this bond is in the valence band. The electron of the H atom finds place on the antibonding combination of the sp^3 hybrids of its neighbors, so that the H atom is at the node of this orbital. The corresponding

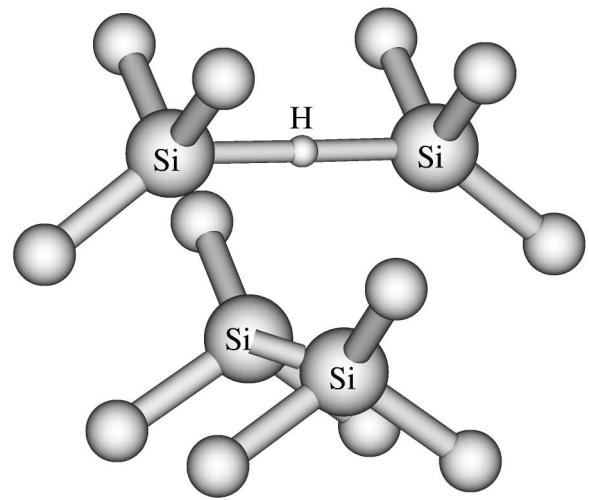


FIG. 1. The structure of the $V_C + H$ complex in $3C$ -SiC.

singly occupied one-electron level is about 1.5 eV below the conduction band edge, E_C (after correction for defect level dispersion and LDA gap error). In addition, a doubly occupied one-electron energy level, corresponding to the long bond between the other two Si neighbors is somewhat above the valence band edge, E_V , of the perfect SC.

The neutral $[V_C + H]^0$ system has a total spin of $S = 1/2$, i.e., should be observable by paramagnetic resonance. $[V_C + H]^+$ is diamagnetic and has the same structure as the neutral defect (0.3 eV more stable than the configuration with the single, "normal" Si-H bond). The hydrogen has a doubly occupied level in the gap, so another paramagnetic state, $[V_C + H]^{2+}$ can be expected. In the double positive state, the two configurations are nearly equally stable (within 0.05 eV). In this case the singly occupied level is at the center of the gap. Further ionization ($3+$) makes the configuration with a weak single Si-H bond (and three empty dangling bonds in C_{3v} symmetry) stable, i.e., the $V_C + H$ system is bistable. We have calculated the relative stabilities of the different charge states as a function of the Fermi-level position (see Fig. 2).

The $2+$ charge state is not stable for any Fermi level position, i.e., the system shows negative U behavior. The accuracy of these results is primarily influenced by the fact that a non-spin-polarized calculation may underestimate the relative stability of a spin-half system by as much as 0.1–0.3 eV. The double positive charge state is, however, definitely unstable even if this relatively large error margin is taken into account. (It should have been calculated to be more stable by at least 0.7 eV relative to the singly positive charge state for positive U behavior.) The calculated ($3+ / 1+$) occupation level is about 1.4 eV above E_V . The lack of spin polarization influences also the calculated ($+ / 0$) occupation level. We estimate it to be 1.8–2.0 eV above E_V . It is interesting to compare $[V_C + H]$ in a given charge state to V_C with the same charge plus 1 electron.

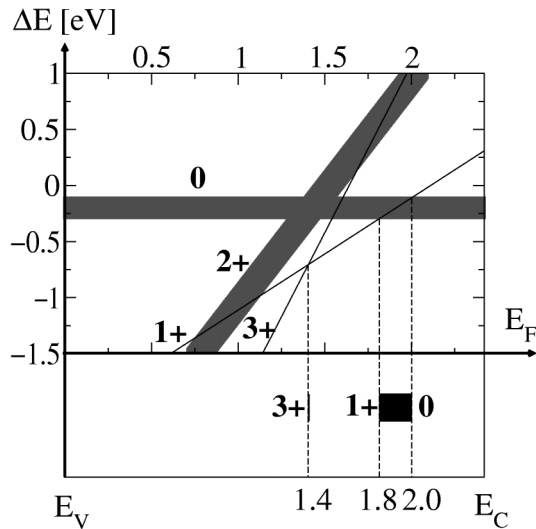


FIG. 2. The relative stability and occupation levels of the various charge states of the $V_C + H$ complex in 3C-SiC. The thickness of the lines represents the uncertainty due to the neglect of spin polarization.

We obtain negative U behavior in this case as well but the stability deficit of the singly positive charge state relative to the neutral one is only 0.3 eV. This may be covered by our error margin. The calculated $(2+/0)$ occupation level for $[V_C]$ is about 2.0 eV, while the $(0/-)$ level is 2.1–2.3 eV above E_V . The symmetry changes from T_d through D_{2d} to C_{2v} . (The $(2+/+)$ occupation level for $[V_C]$ with correction for the dispersion but not for the gap was 1.74 eV in Ref. [23] to be compared to our 1.71 eV.) The doubly occupied one-electron level of V_C^0 is 1.5 eV above E_V .

We have calculated the localization of the unpaired spin and the s/p ratios in MCM for $[V_C + H]^0$ and compared with the values calculated for V_C^- , which resembles it closely. Both systems have C_{2v} symmetry in 3C-SiC, with one electron in the antibonding combination of the dangling bonds of two Si neighbors. On these latter the localization is $\eta^2 = 32\%$ (30%) (on each atom), with an s/p ratio of 18/82 (25/75). The first values refer to $[V_C + H]^0$ (with data for V_C^- in parentheses). The localization of the unpaired spin is 2% (3%) on each of the other two Si neighbors, and about 18% (17%) on the carbon second neighbors together. (The restriction of the cluster size on the delocalization of the defect orbitals can be judged by comparing the value calculated for V_C^+ , $\eta^2 = 16\%$ on each of the Si neighbors, to the one deduced from experiment [24], 7%. The s/p ratio is, however, well reproduced: 16/84 vs 19/81.)

In the neutral charge state the Si-H-Si unit has an asymmetric and a symmetric stretch mode at 1570 and 991 cm^{-1} , respectively. Both are IR and Raman active. In the singly positive charge state, the loss of an electron from an antibonding orbital stiffens the stretch modes to 1770 and 1189 cm^{-1} . In the doubly positive charge

state, the two-center Si-H bond is characterized by a normal Si-H stretch mode of 2072 cm^{-1} , while in the triply positive state this bond becomes so weak that the corresponding LVM mixes with the continuum.

Another consequence of the three-center bonding is that only two H atoms can find place in a carbon vacancy. Introducing a second hydrogen establishes another three-center bonded configuration between the other two Si neighbors of the vacancy. The system is a biradical (two electrons with opposite spin on two spatially orthogonal antibonding orbitals) with D_{2d} symmetry. Accordingly, the system is a double donor with a doubly degenerate e state in the upper half of the gap. A biradical is beyond the scope of a one-electron theory, like LDA, so we have calculated the triplet state of the defect instead (two electrons with parallel spin on two spatially orthogonal antibonding orbitals). The total energy of a unit (supercell or cluster) with this $V_C + 2H$ complex plus another with V_C is higher by only ~ 0.1 eV than twice the energy of a unit with $V_C + H$ (in both types of calculations), so the occurrence of both complexes can be expected. Since both $V_C + nH$ complexes are donors and the capture of three hydrogens is energetically not feasible, V_C cannot be passivated by hydrogens.

The geometry of the $V_C + 2H$ complex differs from that of $V_C + H$ also by the fact that the Si-H-Si bridge is puckered: the angle being 156°. This softens the degenerate asymmetric stretch modes of the two Si-H-Si units and gives rise to a strong splitting between the symmetric and antisymmetric combination of the two symmetric ones. (The H-H distance is 1.615 Å.) The calculated frequencies for the asymmetric stretch modes (both IR and Raman active) and the (Raman active) symmetric combination of the symmetric ones are shown in Table I in the triplet neutral and in the (singlet) double positive charge state, and also for partial and full D \rightarrow H substitution. The values are again far from typical Si-H stretch modes.

In summary, we find that $V_C + nH$ ($n = 1, 2$) complexes may be created during SiC growth in hydrogen ambient. These complexes have donor character and their properties change strongly with charge state. Based on symmetry and the apparent hyperfine interaction with only two equivalent Si atoms, the carbon vacancy related paramagnetic center EI1, seen in p -type electron-irradiated material [25], could be assigned to both $[V_C + H]^0$ and

TABLE I. The effect of isotope substitution on the local vibration mode frequencies of $V_C + 2H$ in the neutral (triplet) and in the doubly positive charge states in cm^{-1} .

Charge	Mode	HH	DH	DO
$[V_C + 2H]^0$	asymm.	976	797	730
	asymm.	976	975	730
	symm.	1332	1177	952
$[V_C + 2H]^{2+}$	asymm.	1132	909	900
	asymm.	1132	1125	900
	symm.	1205	1067	884

V_C^- . The vibration spectrum of hydrogenated SiC samples contains a wealth of bands in the range given by our calculations. The assignment of these features is under way by the Linköping group. Hydrogen related deep level transient spectroscopy peaks could not be observed in electron-irradiated and deuterium implanted 6H SiC [26]. The question arises how stable are these complexes and how kinetic reasons influence their formation. H has a $+/-$ occupation level at $E_F = E_V + 2.3$ eV [13]. Since V_C becomes neutral at $E_F = E_V + 2.0$ and stays so up to $E_F = E_V + 2.1$ or 2.3 eV (depending on our spin polarization error), a narrow window exists for the Fermi level where H (positive) and V_C (neutral) are not in the same charge state. The binding energy between them is 2.4 eV [13]. This is less than the binding energy of V_{Si} and H: 3.3 eV (4.0 eV) between neutral (negative) V_{Si} and H^+ [27]. However, under growth conditions the formation of $V_C + H$ is still more favorable than that of $V_{Si} + H$ by 0.7 eV in carbon-rich environment and by 2.0 eV in silicon-rich environment. Once created, the relatively strong binding energy (2.4 eV) can maintain the $V_C + H$ defect [13].

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