

Isolated oxygen defects in 3C- and 4H-SiC: A theoretical studyA. Gali,¹ D. Heringer,¹ P. Deák,¹ Z. Hajnal,² Th. Frauenheim,³ R. P. Devaty,² and W. J. Choyke³¹*Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8., H-1111, Budapest, Hungary*²*Theoretische Physik, Universität Paderborn, D-33098 Paderborn, Germany*³*Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

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Ab initio calculations in the local-density approximation have been carried out in SiC to determine the possible configurations of the isolated oxygen impurity. Equilibrium geometry and occupation levels were calculated. Substitutional oxygen in 3C-SiC is a relatively shallow effective mass like double donor on the carbon site (O_C) and a hyperdeep double donor on the Si site (O_{Si}). In 4H-SiC O_C is still a double donor but with a more localized electron state. In 3C-SiC O_C is substantially more stable under any condition than O_{Si} or interstitial oxygen (O_i). In 4H-SiC O_C is also the most stable one except for heavy n -type doping. We propose that O_C is at the core of the electrically active oxygen-related defect family found by deep level transient spectroscopy in 4H-SiC. The consequences of the site preference of oxygen on the SiC/SiO₂ interface are discussed.

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I. INTRODUCTION

There has been considerable interest in recent years in silicon carbide (SiC) as a wide band-gap semiconductor material for high-temperature, high-frequency, and high power applications. Because of recent advances in crystal growth it is now possible to produce both epitaxial and bulk SiC material of high quality. An important switching device is the metal-oxide-semiconductor field-effect transistor. During oxidation or other processing steps oxygen impurities may enter the SiC crystal. Even though the oxygen solubility in SiC is low,¹ the understanding of its behavior is important from the viewpoint of incorporation during oxidation. It is well known that in other semiconductors oxygen can form electrically active defects, like the A center² and the thermal double donors in silicon.³ Therefore, the behavior of oxygen in bulk SiC is also of interest.

SiC has many polytypes with a common two-dimensional (hexagonal) unit cell but different stacking sequences of the tetrahedrally bonded Si/C bilayers in the third dimension. The most important polytypes are the hexagonal 4H and 6H-SiC and the zinc-blende (cubic) 3C-SiC. The band gaps are 3.3, 3.0, and 2.4 eV, and the numbers of basis atoms in the primitive cell are 8, 12, and 2, respectively. According to the local environment up to third neighbors, a so-called quasicubic (k) site and a quasihexagonal (h) site can be distinguished in 4H-SiC. 6H-SiC has two different quasicubic sites: k_1 , k_2 . This paper aims to investigate oxygen in 3C- and 4H-SiC. Due to the common first- and second-neighbor bonding environments in the three polytypes, defects with strongly localized states may have very similar properties. Experimental data on oxygen in 4H- and 6H-SiC show little difference.^{4,5}

Only limited information is available about oxygen in bulk SiC. Dalibor *et al.* implanted O^+ into chemical vapor deposited (CVD) n - and p -type 4H and 6H-SiC epitaxial layers.^{4,5} Deep level transient spectroscopy (DLTS) has shown that two groups of shallow donorlike oxygen-related centers had been created with ionization energies at $E_v + (2.85-2.87)$ eV and $E_v + (2.80-2.82)$ eV in 6H, and at

$E_v + (2.99-3.03)$ eV and $E_v + (2.84-2.88)$ eV in 4H-SiC. The values of the ionization energies were dependent on the implanted oxygen dose and on the annealing temperature. These facts imply that these oxygen-related donor centers may originate from defect aggregates which contain oxygen atoms in the core region. Three deep acceptorlike oxygen-related centers with levels in the range between $E_v + 2.4$ and $E_v + 2.6$ eV have been found both in 6H- and 4H-SiC samples implanted with oxygen.^{4,5} It was speculated that the origin of these levels might be oxygen at the silicon site in analogy to the A center in silicon. The same donor and acceptor levels have also been found in CVD epitaxial layers grown in an environment containing CO₂ gas.⁶ The concentration of the acceptor defects were, however, three orders-of-magnitude lower than in the implanted samples. Aboelfotoh and Doyle⁷ found a donorlike level at $E_v + 2.13$ eV in 6H-SiC with DLTS, assigning it to an oxygen+carbon vacancy complex. This assignment was based on the observation that after heat treatment the concentration of this DLTS center has increased simultaneously with the decrease of another which was believed to be due to the isolated carbon vacancy. Since the new level has shown no correlation with hydrogen introduced intentionally into the sample, Aboelfotoh and Doyle proposed oxygen as another feasible impurity trapped by the carbon vacancy to be responsible for the new donorlike level. However, no correlation with oxygen has been shown. Oxygen could suppress the formation of vacancy-type defects after O^+ implantation into 6H-SiC as shown by monoenergetic positron beam measurements.⁸ The trapping of oxygen in vacancies was proposed during this process producing higher quality of SiC but neither the structure of these oxygen-related defects nor their electronic properties were reported.

The only theoretical studies we are aware of in SiC considered oxygen solely as an interstitial in the neutral charged state, using molecular cluster and supercell models.^{9,10} Di-Ventra and Pantelides found that oxygen clustering in the (110) plane in 3C-SiC could be energetically feasible in a manner very similar to the possible core of the thermal double donors in silicon.¹⁰ In an earlier work we calculated

TABLE I. The calculated total energy of the oxygen molecule as a function of cutoff of the plane-wave expansion.

Kinetic-energy cutoff (Ry)	Total energy (eV)
30	-845.285
36	-853.361
48	-860.552
64	-862.266
80	-862.345
100	-862.373

interstitial and substitutional oxygen in the neutral state in a molecular cluster model of 3C-SiC,¹¹ but neither relative stabilities nor occupancy levels were given.

The present paper investigates the isolated oxygen defects in 3C- and 4H-SiC, especially the electrically active ones. We will show that the formation of O_C is the most likely among the isolated oxygen defects and it may be responsible for the donor centers found in 4H-SiC. The paper is organized as follows: the calculational methods will be presented in section II, while the results for 3C- and 4H-SiC will be given in Secs. III and IV, respectively, and discussed in Sec. V.

II. MODEL AND CALCULATIONAL METHOD

Ab initio calculations based on density-functional theory in the local-density approximation¹² (LDA) with the exchange correlation of Ceperley and Alder¹³ were carried out in a supercell (SC) model, with a plane-wave basis using the FHI98MD code,¹⁴ to determine the equilibrium configurations, relative stabilities, and occupancy levels of oxygen defects. In the SC calculations 3C-SiC was modeled by a 128-atom-fcc, and 4H-SiC by a 96-atom-hcp unit cell. Norm-conserving Troullier-Martins pseudopotentials¹⁵ were used. It has already been shown¹⁶ that in this case a kinetic-energy cutoff of 30 Ry in the plane-wave expansion is sufficient to describe the properties of perfect SiC, however, the extremely oscillating nature of oxygen valence orbitals make a careful test of the cutoff necessary. We have investigated both the pseudopotential and the plane-wave basis on the O_2 molecule and on crystalline α -quartz. First, the energy of the oxygen molecule (calculated in a sufficiently large supercell) was obtained as a function of the cutoff from 30 Ry up to 100 Ry. The difference in the total energy for a cutoff of 64 Ry and 80 Ry was less than 0.08 eV (see Table I). Then we have carried out a geometry optimization for α -quartz with a 64 Ry cutoff. The resulting Si-O distances, the Si-O-Si angle, and the calculated heat of formation agreed with the experimental values within 1%, 1.3%, and 2.3%, respectively. The defect calculations in SiC were then carried out using this 64 Ry cutoff. Summations over the reduced Brillouin zone of the supercell were carried out using $2 \times 2 \times 2$ and $3 \times 3 \times 3$ Monkhorst-Pack (MP) schemes.¹⁷ The $3 \times 3 \times 3$ set was only applied for defects with effective-mass-like states.¹⁸ Tests with the O_C^{2+} defect (dipositive oxygen on the C site, with no occupied levels in the gap) showed a difference of <0.05 eV

TABLE II. Comparison of the experimental and the calculated occupation levels of interstitial hydrogen and phosphorus next to a vacancy in silicon without and with corrections (see text). The values refer to the valence-band maximum in eV.

Defect	No correction	Corrected	Experiment
$H_i (+/0)$	0.46	1.00	0.96 ^a
P-V (0/-)	0.23	0.58	0.68 ^b

^aSee Ref. 21.

^bSee Ref. 22.

in total energy between the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ sets. In the case of defects with occupied states in the gap the error due to defect band dispersion is corrected for, as described in Ref. 19. Using the total energy of the perfect and defective supercells, the formation energy and relative stabilities of the defects can be calculated. Comparing the energy of different charge states yields the Fermi-level position, where the charge state of the defect changes (i.e., the occupation levels). A major problem is that the width of the band gap is always severely underestimated in density-functional theory. That influences the energy of the electrons on gap levels and, thereby, the total energy as well. An *a posteriori* correction was applied to make up for this LDA “gap error” as explained in Ref. 19. Another source of inaccuracy in the relative stabilities arises because of the limitations of our plane-wave supercell code to spin-unpolarized calculations and because of the lack of a charge correction.²⁰ (The energies of isolated atoms in vacuum were, however, determined with spin polarization.) Since very few deep level defects have as yet been identified in SiC, in order to verify our method we have calculated the well-known and experimentally measured occupation levels of two defects in silicon: the (+/0) level of interstitial hydrogen (E_3' DLTS signal of H_i)²¹ and the (0/-) level of the E center originating from phosphorus next to a vacancy (P-V).²² We have used a 128-atom-fcc supercell with a $2 \times 2 \times 2$ k -point set and 32 Ry cutoff which provided convergent results for these defects. The calculated occupation levels without and with corrections compared to the experimental ones can be seen in Table II. The values with the *a posteriori* band-gap and dispersion corrections are in reasonable agreement (~ 0.1 eV) with the experimental ones.

The geometries of minimal energy for the oxygen defects were sought by allowing four shells of host atoms around the defect to relax and reconstruct in the 128-atom SC, until all the forces were below 0.0005 hartree/bohr. The 96-atom 4H supercell allows only the relaxation of three shells without distorting the lattice structure. The third-neighbor relaxation lowers the total energy of oxygen substitutional at the carbon site and interstitial oxygen by only <0.01 eV and <0.1 eV, respectively (with respect to second-neighbor relaxation). Therefore, this restriction does not cause a significant error.

The stability of various oxygen defects can be compared by defining a formation energy as (see, e.g., Refs. 23 and 24)

$$\begin{aligned}
 E_{\text{form}}^q(n_{\text{Si}}, n_{\text{C}}, n_{\text{O}}; \mu_{\text{Si}}, \mu_{\text{C}}, \mu_{\text{O}}, E_{\text{F}}) \\
 = E_{\text{tot}}^q(n_{\text{Si}}, n_{\text{C}}, n_{\text{O}}) - n_{\text{Si}}\mu_{\text{Si}} - n_{\text{C}}\mu_{\text{C}} - n_{\text{O}}\mu_{\text{O}} + qE_{\text{F}},
 \end{aligned}
 \tag{1}$$

where E_{tot}^q is the total energy of a supercell consisting of n_{Si} silicon, n_{C} carbon, and n_{O} oxygen atoms with the defect in the q charge state. E_{tot}^q is obtained as the total energy of the supercell. E_{F} is the Fermi energy or electron chemical potential, i.e., the energy of the reservoir from which electrons are taken: this depends on the doping level and temperature of the real crystal. E_{F} changes from the top of the valence band (E_{v}) to the bottom of the conduction band (E_{c}), i.e., $(E_{\text{F}} - E_{\text{v}})$ varies from 0.0 eV to 2.42 eV (Ref. 25) and 3.27 eV (Ref. 26) in 3C-SiC and in 4H-SiC, respectively. The chemical potentials of silicon, μ_{Si} , and of carbon, μ_{C} , are connected. Under stoichiometric conditions $\mu_{\text{Si}} = \mu_{\text{Si}}^{\text{bulk}} - \frac{1}{2} \Delta H_{\text{f}}^{\text{SiC}}$ and $\mu_{\text{C}} = \mu_{\text{C}}^{\text{bulk}} + \frac{1}{2} \Delta H_{\text{f}}^{\text{SiC}}$, where $\Delta H_{\text{f}}^{\text{SiC}}$ is the formation enthalpy of SiC (for details, see Ref. 19).

The determination of μ_{O} requires more consideration. Oxygen-related DLTS signals were found in samples which were implanted with oxygen^{4,5} or were CVD grown in a CO₂-containing environment.⁶ Only the latter can be regarded as a quasiequilibrium process but it is very difficult to estimate μ_{O} in a mixture of silane, propane, and CO₂. Instead, we will consider equilibrium with molecular and atomic oxygen at different pressures and temperatures. The value of μ_{O} will then be calculated as described in Ref. 19 for hydrogen.

III. RESULTS IN 3C-SiC

A. Oxygen at the carbon site

Our calculations indicate that O_C is an on-center defect with T_d symmetry. The Si-O distance is 2.00 Å and the second-neighbor bonds shorten to 1.83 Å from the original 1.88 Å. This configuration is similar to that of sulphur in silicon. Although oxygen is smaller than sulphur, so is the interatomic distance of SiC with respect to that of Si. The Si-O distances are very long compared to normal Si-O bonds, indicating a stronger than usual ionic nature of the bonds, which can be the consequence of the fourfold coordination and the fact that the SiC crystal is partially ionic in the first place. This is corroborated by the electron-density map shown in Fig. 1. As can be seen, there is still some covalent component in the Si-O bonds. Analyzing the electronic structure in terms of a defect-molecule model, the quasiautomatic s and p states formed by the dangling bonds around the vacancy (containing four electrons) interact with the s and p orbitals of the oxygen atom (containing six electrons), as can be seen in Fig. 2. The resulting a_1 and t_2 bonding orbitals accommodate eight electrons. The localized antibonding a_1^* one-electron level is located 0.6 eV above the conduction-band edge, therefore an effective-mass-like (EMT) orbital gets occupied instead. Therefore, O_C is a double effective-mass-like donor in 3C-SiC, like sulfur in silicon. The one-electron level of the defect is at $E_{\text{c}} - 0.2$ eV. One would expect that oxygen should reconstruct into C_{2v} symmetry by moving off-center in the $\langle 001 \rangle$ direction like it does in silicon.²⁷ We have found a metastable state where the oxygen bonds to two silicon atoms (the bond length and the angle of the bridge are 1.75 Å and 138°, respectively), but this structure is about 1.2 eV higher in total energy than the on-center

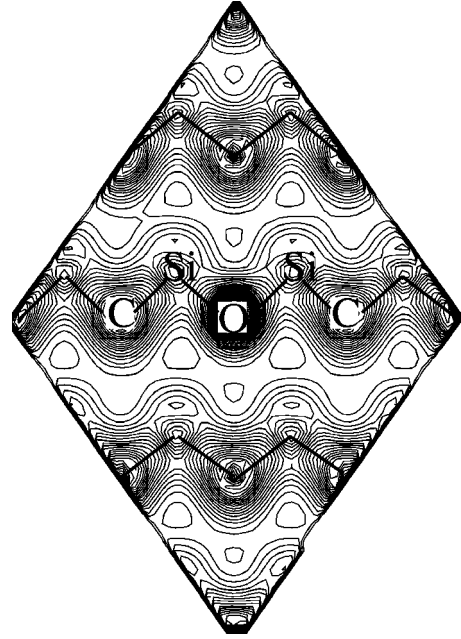


FIG. 1. The calculated total electron-density map of O_C in the (110) plane of 3C-SiC.

configuration. A calculation with 30 Ry cutoff in the plane-wave expansion gives 1.4 eV for this difference. Therefore, further increase in the cutoff is unlikely to change the energy sequence of these configurations. In the C_{2v} configuration the electrons of the two lone pairs of oxygen are repelled by the electrons of the dangling bonds of the other two Si atoms around the vacancy (the first-neighbor distances are much shorter in SiC than in silicon) which is energetically unfavorable.²⁸

In the single positive charge state no metastable state was found, so this is an on-center defect with T_d symmetry. The Si-O distance is slightly shorter (1.99 Å) than in the neutral

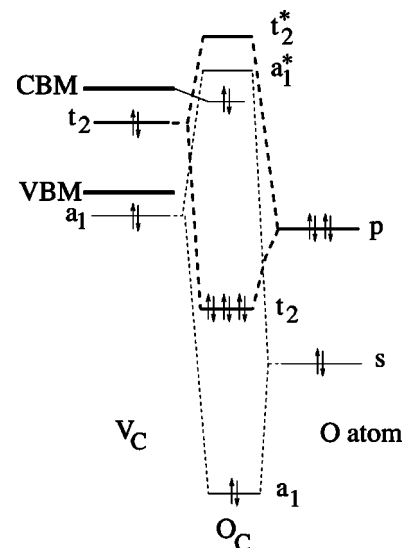


FIG. 2. The schematic bonding diagram between the carbon vacancy, i.e., Si dangling bonds, and the oxygen atom forming the O_C defect in 3C-SiC.

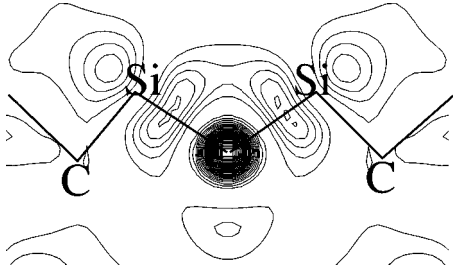


FIG. 3. The spin density in the vicinity of O_C (in the middle of the figure) projected onto the (110) plane of 3C-SiC.

state. In the case of O_C^{2+} , the Si-O distance is further shortened (1.98 Å) but the geometry is essentially the same as for the neutral and the single positive defect.

The occupation levels of the O_C double donor are at $E(2+/+) = E_v + 2.13$ eV and at $E(+/0) = E_v + 2.09$ eV. This would correspond to negative- U behavior but we note that the lack of spin polarization underestimates the stability of the singly positive charge state by at least 0.1 eV. Therefore, we expect normal, positive- U behavior for this defect. From the distribution of the absolute square of the wave function (see Fig. 3) it seems that the spin localization on the oxygen atom in O_C^+ should be sufficient to be detectable by electron paramagnetic resonance. The shape of the distribution on oxygen is spherical, therefore, the Fermi-contact term of the hyperfine interaction must be much bigger than that of the dipole-dipole term.

B. Oxygen at the silicon site

We have also found two metastable configurations for oxygen at the silicon site (O_{Si}) in the neutral state. The more stable one has C_{2v} symmetry; the oxygen moves out of the center by 0.37 Å in the $\langle 001 \rangle$ direction, forming a bridge with two carbon atoms. The C-O-C angle is 123° and the C-O bond length is 1.62 Å. The other two carbon atoms relax outward, such as in the case of the Si vacancy (V_{Si}) of SiC.^{23,19} The on-center configuration with T_d symmetry is only 0.14 eV higher in energy than the off-center configuration. The C-O distances in the on-center configuration are equal to 1.92 Å and there is very little bonding between O and the four C neighbors. The reason is that the carbon and oxygen have higher electronegativity than silicon, so the carbon atoms around the oxygen and the O atom itself have negative net charges, thereby repelling each other. The reconstruction to C_{2v} symmetry lowers the energy but the energy gained by forming the C-O bonds is mostly compensated by the unfavorable closeness of the other two carbon atoms repelled by the oxygen lone pairs. In both configurations there is a double occupied level in the gap at $E_v + 1.0$ and at +1.1 eV for C_{2v} and T_d , respectively. Therefore, O_{Si} is a hyperdeep double donor (or rather a double hole trap). In case of the positively charged O_{Si}^+ , the on-center site is already the most stable configuration with a C-O distance of 1.89 Å. In the case of O_{Si}^{2+} the C-O distance is shortened further to 1.85 Å. The $(2+/+)$ and $(+/0)$ occupation levels are at $E_v + 0.6$ and 0.8 eV.

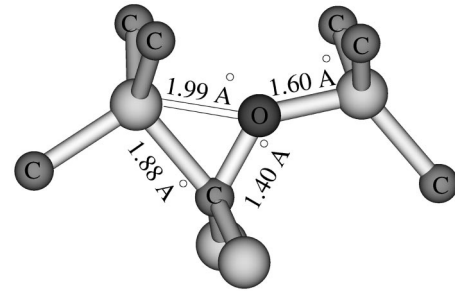


FIG. 4. The optimized geometry of O_i in 3C-SiC. (The unlabeled atoms are Si atoms.)

The silicon site for oxygen turns out to be so high in energy that it is worth investigating whether the oxygen and its first-neighbor C atom would change their positions to create an $O_C + C_{Si}$ complex. It is known that the V_{Si} itself is a metastable (or bistable) defect with $V_C + C_{Si}$ in SiC.^{29,16} The $O_C + C_{Si}$ complex has C_{3v} symmetry. The calculated total energy of this defect is, indeed, 4.0 eV lower than that of O_{Si} . $O_C + C_{Si}$ is a double donor where the donor level is at $E_v + 2.3$ eV. The donor state is localized in the vicinity of oxygen in this case.

C. Interstitial oxygen

Interstitial oxygen has already been investigated by several theoretical groups.⁹⁻¹¹ The geometry obtained in the present calculation is practically the same as the result of earlier calculations (see Fig. 4). The structure has C_{1h} symmetry. The complicated bonds between oxygen, carbon, and the two silicon atoms provide two fully occupied levels in the band gap very close to the valence-band top (within 0.1 eV).

D. Relative stabilities of the isolated oxygen defects in 3C-SiC

The formation energy of the different isolated oxygen defects as a function of the chemical potential of oxygen under stoichiometrical conditions can be seen in Table III. The formation of O_C is the most feasible energetically, while that of O_{Si} seems quite unlikely in equilibrium. The relation of the concentrations of the isolated electrically active oxygen defects should be $[O_C] \gg [O_C + C_{Si}] \gg [O_{Si}]$. The differences between the formation energies are so big that this relation can be predicted for all the polytypes of SiC.

TABLE III. Formation energies of neutral oxygen defects under stoichiometric conditions in 3C-SiC as a function of chemical potential of oxygen in eV.

Complex	E_F
O_C	$-432.5 - \mu_O$
O_i	$-431.3 - \mu_O$
$O_C + C_{Si}$	$-428.9 - \mu_O$
O_{Si}	$-424.9 - \mu_O$

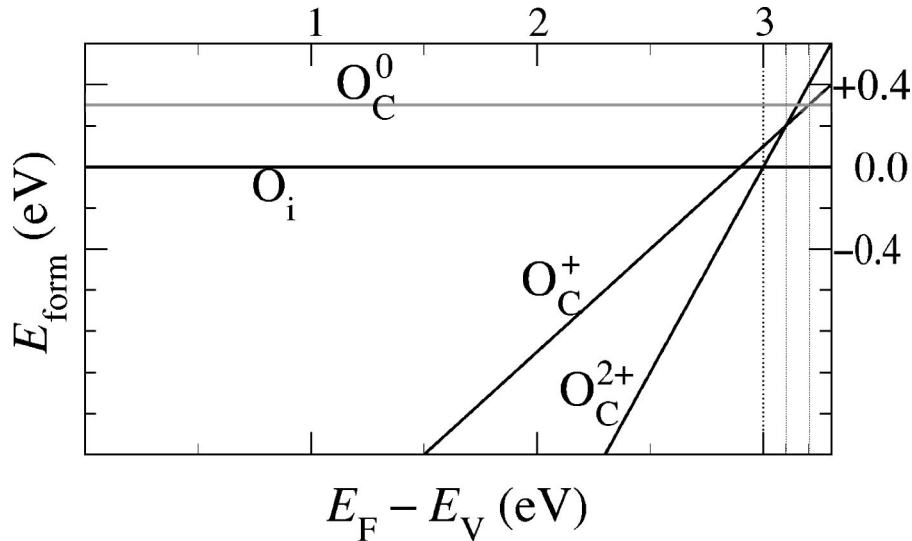
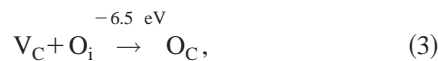
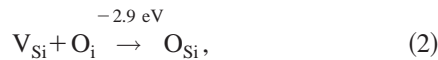


FIG. 5. Formation energies of the various charge states of O_C at the k site as a function of the position of the Fermi level in bulk grown 4H-SiC with respect to O_i .

If oxygen is implanted, also vacancies are created. After annealing, interstitial oxygen can be trapped in them. The binding energies between the vacancies and oxygen are the following:



i.e., O_i prefers the C vacancy against the Si vacancy by 3.6 eV.

IV. RESULTS IN 4H-SiC

Since substitutional oxygen on the C site appears to be electrically active, it is interesting to investigate it in 4H-SiC as well. Earlier calculations have shown²³ that for defects with localized electron states neither the position of the occupation levels (with respect to the valence-band edge) nor the formation energy differ much between polytypes. Considering this and regarding the high formation energy of oxygen on the Si site in 3C-SiC, we dropped that defect from further investigations in 4H-SiC. On the other hand, a significant difference can be expected in the case of O_C since the a_1^* level of O_C^0 in 3C-SiC is at $E_v + 3.0$ eV which would fall into the band gap of 4H-SiC, therefore this level can be occupied instead of an EMT state. We have, therefore, calculated O_C in 4H-SiC at the k and h sites. For comparison, we calculated also O_i at the k site.

The formation energy of O_C^0 is 1.8 eV higher in 4H-SiC than in 3C-SiC because the one-electron donor level occupied by two electrons is situated about 1.0 eV higher in 4H-SiC than in 3C-SiC. Due to the higher formation energy of O_C^0 in 4H-SiC, in the on-center configuration this is a localized a_1^* state which makes this configuration unstable. The oxygen moves off-center. The double occupied level is

at $E_v + 3.2$ eV (for the k site). O_C is thus a double donor in 4H-SiC but not an effective-mass-like one as in 3C-SiC. The possible charge states for O_C in 4H-SiC are the (2+), (+), and (0). The symmetry of O_C^{2+} is C_{3v} while that of O_C^+ is similar to O_C^0 (C_{1h}). In the paramagnetic (1+) state the spin density is partly localized on oxygen. The spherical distribution indicates a considerable Fermi-contact hyperfine interaction with the hyperfine active oxygen nucleus similar to the case of 3C-SiC. The spin density is, however, mainly localized on the p orbitals of silicon atoms around the oxygen. The (2+/+) and (+/0) occupation levels at the k site are at $E_v + 3.1$ eV and $E_v + 3.2$ eV.

The difference between the k and h sites were examined for O_C^{2+} . The total energy was lower at the h site by 0.11 eV and the Si-O bond lengths were about the same.

As a consequence, the formation of the electrically inactive O_i is now more feasible in heavily n -type 4H-SiC than that of O_C (see Fig. 5). If oxygen enters SiC by means of implantation, after the heat treatment interstitial oxygen and the vacancies can diffuse and according to Eqs. (2) and (3) O_i can be captured by vacancies. Equation (3) modifies to about -4.7 eV in 4H-SiC.

To estimate the amount of oxygen incorporation into 4H-SiC, we have considered two cases: oxygen as a contaminant in bulk growth assuming a partial pressure of 10^{-10} atm atomic oxygen at 2400 °C, and 0.1 atm molecular oxygen at 1500 °C, in order to give an estimate for the CVD samples grown in the presence of CO_2 . (The CVD growth was performed with a pressure of 1 atm, mixing CO_2 to the gas flow of H_2 , SiH_4 , and C_3H_8 . Assuming a partial pressure of 0.1 atm of O_2 in the chamber is a rough estimate, but the result is relatively insensitive for changes between 0.01 and 0.3 atm.) The corresponding values for μ_O are -439.32 and -430.99 eV, respectively. The formation energy for all the oxygen defects is too high to have a measurable contamination in bulk grown SiC. In the case of CVD growth with CO_2 , the oxygen concentration of the samples

TABLE IV. The concentration of O_C in $4H$ -SiC as a function of dopant concentration assuming that the source of oxygen is the O_2 gas at the temperature of 1500°C and at pressure of 0.1 atm. The n -type dopant is nitrogen and the p -type dopant is aluminum. N_D is the concentration of nitrogen while N_A is the concentration of aluminum.

Dopant concentration (cm^{-3})	Concentration of O_C (cm^{-3})
$N_A = 10^{19}$	4.7×10^{18}
$N_A = 10^{18}$	8.3×10^{17}
$N_A = 10^{17}$	2.4×10^{17}
$N_A = 10^{16}$	2.4×10^{17}
$N_A = 10^{15}$	2.3×10^{17}
$N_D = 10^{17}$	2.2×10^{17}
$N_D = 10^{18}$	2.3×10^{16}
$N_D = 10^{19}$	3.5×10^{15}

will, however, not be negligible. Using the formation energies the concentration of the defects (N_i) can be determined by

$$N_i = N_i^0 e^{-E_{\text{form}}^{q_i} / k_B T}, \quad (4)$$

where N_i^0 is the concentration of sites in the perfect lattice for the given defect and k_B is the Boltzmann constant. The formation energy of O_C in its charged states is dependent on the position of the Fermi level which depends on the temperature and the concentration of free carriers (due to both the dopants and the oxygen defects themselves). The position of the Fermi level (and the corresponding defect concentration), therefore, should be calculated self-consistently using the neutrality condition. Details of the method can be found in Ref. 19. The values for the effective mass of electrons and holes in $4H$ -SiC have been taken from Refs. 30 and 31.

The concentration of O_C as a function of dopant concentration can be seen in Table IV. The concentration of the electronically inactive O_i does not depend on the position of the Fermi level but it is several orders-of-magnitude lower than that of O_C except for highly n -doped samples with a net donor concentration above 10^{19}cm^{-3} . Table IV predicts an oxygen concentration of 10^{16} – 10^{17} at 1500°C assuming 0.1 atm O_2 in the reactor chamber, except for heavy doping. The O_C donor concentration is sufficient to compensate p -type doping.

V. DISCUSSION

The calculated formation energies indicate that under equilibrium conditions only the concentration of O_C can be significant, by all means much higher than that of O_{Si} in all polytypes. O_i is easily captured by vacancies. This agrees with the experimental finding that the concentration of single vacancies can be decreased by introducing oxygen.⁸ Since only DLTS measurements in hexagonal polytypes have been correlated with the presence of oxygen, we focus the discussion on the electrically active O_C defect in $4H$ -SiC. O_C in $4H$ -SiC at the k site is a double donor with $(2+/+)$ and

$(+/0)$ occupation levels at $E_v + 3.1$ eV and at $+3.2$ eV, respectively. These values agree reasonably well with the data measured by DLTS at 2.99 – 3.03 eV in $4H$ -SiC. The series of DLTS peaks is likely to have originated from a defect aggregate which contains oxygen. Based on (i) the agreement between the measured and calculated occupation levels, (ii) the fact that the observed DLTS centers were abundant *both* in ion implanted SiC and in the samples grown in CO_2 , and (iii) the fact that the calculated formation energy is lowest among the isolated electrically active defects, we are strongly inclined to suggest O_C as the core of the donorlike, oxygen-related DLTS centers observed in Refs. 4–6. The CVD samples grown in CO_2 had a nitrogen concentration of 2 – $4 \times 10^{18} \text{cm}^{-3}$ and the oxygen donor concentration was estimated to be $< 5 \times 10^{17} \text{cm}^{-3}$.⁶ Our calculated oxygen concentrations satisfy this condition. (Increasing the O_2 partial pressure to 0.3 atm still gives only $4.6 \times 10^{16} \text{cm}^{-3} O_C$.) The p -type samples implanted by oxygen showed full compensation of the doping.^{4,5} This is in agreement with our calculated relation of the concentrations of O_C and the acceptors.

The very high formation energy (obtained in $3C$ -SiC) indicate that the concentration of O_{Si} should be under the detection limit, whereas the acceptorlike DLTS levels appear in CVD grown samples.⁶ This implies that O_{Si} is not the origin of the acceptor centers found in hexagonal polytypes by DLTS in Refs. 4–6. (The electronic structure obtained in $3C$ -SiC for O_{Si} also does not support such a model.) More complex defects should be involved in that case than the isolated oxygen defects.

Our result about the dominance of O_C over O_i (except for heavy n -type doping) may have serious implications on the oxidation behavior of SiC, provided this relation between the formation energies is sustained at the SiC/SiO₂ interface as well (where the relaxational freedom is higher). Consider the case of silicon first. Oxygen prefers the interstitial position in silicon, forming a Si-O-Si bridge which is also the building block of SiO₂. When new oxygen arrives at the Si/SiO₂ interface, the SiO₂ network simply extends deeper into the Si phase. The interface is, therefore, always abrupt chemically, and the oxidation rate is only limited by the oxygen diffusion. In contrast, our calculations indicate that oxygen in SiC prefers the carbon site. Therefore, when oxygen atoms arrive at the SiC/SiO₂ interface, they substitute carbon atoms forming a thin oxygen contaminated Si-rich interface layer which has still to undergo a structural reconstruction to form SiO₂. The presence of such a layer has indeed been observed by x-ray photoelectron spectroscopy (XPS).³² The net chemical composition of this layer should be close to that of SiO, which has a gap between 2 and 3 eV. We believe that the conduction band tail of this layer appears in the upper part of the SiC gap as a near-interface state density.³³ It is known that the density of these interface states can be diminished by a reoxidation anneal.³⁴ It has been shown that at the same time the thickness of the transition layer has also decreased!³² It should be noted that more recent studies claim no change of the states near the band edges.³⁵ To

clarify the situation, further calculations for the interface are in progress.

VI. SUMMARY

Ab initio calculations were carried out on oxygen impurity centers in 3C- and 4H-SiC to obtain their electrical properties. The results were compared to experimental findings. We suggest that the core of the oxygen-related shallow donor centers, observed after oxygen implantation or CVD growth in a CO₂ environment by DLTS, contains oxygen substitutionals at the carbon site. The oxygen-related acceptor centers found under the same conditions cannot be assigned to oxygen at the silicon site. We predict that—unlike interstitial

oxygen in silicon—in SiC oxygen prefers the (carbon) substitutional site. This may be the reason for the transition layer at the SiC/SiO₂ interface, observed by XPS and possibly that of the near-interface traps.

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