

Local electronic structure around vacancies and vacancy–antisite complexes in β -SiC

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Abstract. The local electronic structure around vacancies and vacancy–antisite complexes in cubic SiC has been calculated by means of the LMTO (linear muffin-tin orbital) method and the supercell approach. In order to improve the description of the electronic structure near the energy gap, the orbital-dependent LDA + U potential has been used. Different models for the displacement of the atoms around the defects are discussed. It has been shown that the atoms surrounding a silicon vacancy (V_{Si}) relax outwards from the vacancy, while for a carbon vacancy (V_{C}) a distortion of the tetrahedral arrangement of atoms is the more reliable model. The calculations of the local electronic structure performed for the vacancy–antisite complexes show that the $V_{\text{Si}} + \text{Si}_{\text{C}}$ complex is characterized by a repulsive interaction between the Si_{C} antisite and the three carbon atoms surrounding the vacancy. In contrast, the stability of the $V_{\text{C}} + \text{C}_{\text{Si}}$ complex is determined by the bonding of the atoms surrounding the vacancy. In all cases the appearance of the localized electron state in the middle region of the energy gap is a characteristic feature of the vacancy–antisite complex. Some possible mechanisms of the annealing out of the vacancies in β -SiC are discussed.

1. Introduction

Due to the possible advances in device applications of silicon carbide, the electronic properties of the different phases and polytypes of this material are a subject of considerable interest. In the past few years a great number of theoretical investigations have been devoted to the electronic structure of the perfect SiC crystals [1–8], while the electronic structure around native defects in SiC has received less attention, with the result that an understanding of their effect on the electronic properties has not been achieved.

In [9] we studied theoretically the local electronic structure around antisite defects in cubic (zinc-blende) β -SiC. It was shown that the lattice relaxation around a point defect causes significant changes in the energy distribution of the electron states in the valence band as well as in the conduction band. Unlike the antisite defects, vacancies give rise to localized electron states in the band gap, whose energy positions may also be influenced by the relaxation of the atoms surrounding the vacancy.

Recently, a number of experimental studies on defects in β -SiC have been performed by means of photoluminescence [10, 11], electron paramagnetic resonance [12], optically detected magnetic resonance [13], deep-level transient spectroscopy (DLTS) [14–16], and positron annihilation spectroscopy [17], but the interpretations of the experimental data differ significantly. Due to the localized electron states in the band gap, the presence of carbon

and silicon vacancies could in principle be detected by experiments. However, in [14] it was reported that an epitaxial β -SiC film is free of deep levels in the upper third of the band gap, whereas two deep levels located at 0.34 and 0.68 eV below the bottom of the conduction band were found in [15]. Freitas and Bishop [10] have found a deep acceptor located at 0.47 eV above the top of the valence band.

The electronic structure of native defects in β -SiC has been studied theoretically by means of different methods of calculation. Using a large-cluster recursion method with Slater–Koster parametrization, Li and Lin-Chung [18] have found that C and Si vacancies in β -SiC would behave as acceptors and donors, respectively. However, in later papers, where the *ab initio* pseudopotential method within the supercell approach [19], the tight-binding Green-function method [20], the LMTO Green-function method [21], and the recursion method [22] were used, an opposite behaviour of vacancy states has been reported. In the quoted works, except [19,22], the effects of the lattice relaxation on the local electronic structure were not considered.

Unfortunately, the published information on the local relaxation around vacancies in β -SiC is sparse. We can quote only results of pseudopotential calculations [19], showing that the nearest-neighbour atoms around a carbon vacancy (V_C) relax by only 0.6% of the nearest-neighbour distance, as well as results of molecular dynamics simulations [23], showing that neighbouring atoms relax outwards from the vacancy and that relaxation shifts around the silicon vacancy (V_{Si}) considerably exceed those around V_C . Recently a detailed study of the electronic structure around relaxed vacancies was performed in [24] by means of the *ab initio* pseudopotential method within the supercell approach. There it was shown that the character of the local lattice relaxation is strongly dependent on the charge state of the vacancy.

It should be noted that carbon vacancies were found to be annealed out at relatively low temperatures (about 200 °C) [25] while silicon vacancies are thermally stable defects with a high annealing temperature (at least 750 °C) [13]. Thus it seems to be useful to study what the role of the local electronic structure and interatomic bonding is in this difference in behaviour between the V_C and V_{Si} .

In this work we present the results of a theoretical study of the electronic structure of the β -SiC polytype containing single V_C vacancies and single V_{Si} vacancies as well as vacancy–antisite complexes. The calculations have been performed by means of the LMTO method using the LDA + U approach in the form described in [9]. A supercell approach has been used to describe the crystal structure containing a relaxed atomic configuration around a point defect. The main attention was paid to the changes in the local electronic structure due to the relaxation shifts of atoms surrounding the vacancy, and some possible mechanisms of the annealing out of the vacancies in β -SiC are discussed.

The paper is organized as follows. In section 2 we describe briefly the theoretical aspects and the computational details. In section 3 the calculated local electronic structure around single vacancies is discussed. In section 4 the results for a vacancy–antisite complex are given. Conclusions are drawn in section 5.

2. Structure model and computational details

The theoretical model and the details of the method of calculation have already been given in [9]. Here we describe briefly the most important quantities used.

The atomic structure of β -SiC can be described as a vertical sequence of Si–C bilayers ABCABC... We have chosen a supercell containing 18 atoms (nine Si atoms and nine C atoms in the case of the perfect crystal) in three bilayers. It has been shown in our preceding calculations [9,26] that such a supercell is large enough, and the interaction of point defects located in different supercells can be considered negligible.

The energy band structure has been calculated by means of the self-consistent LMTO method [27, 28] in the atomic sphere approximation and including the combined corrections (ASA + CC). In order to obtain a close-packed structure, empty spheres have been introduced in the interstitial regions, so the total number of spheres in the supercell was 36. The calculations have been performed within the scalar-relativistic formalism for the valence states whereas the full relativistic solutions have been used for the core levels. The exchange and correlation effects have been taken into account by using the local density approximation (LDA) and the von Barth–Hedin parametrization for the exchange–correlation potential [29]. In order to overcome a well-known deficiency of the LDA (the underestimation of the band gap), we have used the LDA + U approach [30] in the form described in [9]. The parameter values $U_p(\text{C}) = 3.78$ eV and $U_p(\text{Si}) = 2.18$ eV were used. The angular momentum expansion of the basis functions was performed up to $l = 2$ for all of the spheres. The electron density of states (DOS) was computed by using the Brillouin zone integration method described in [31] (238 irreducible k -points of Blöchl mesh were used). We have used for the atomic sphere radii the following values: 2.2357 au for Si atoms, 1.9207 au for C atoms, 1.8054 au for empty spheres surrounded by ‘large’ Si atoms, and 2.1016 au for empty spheres surrounded by ‘small’ C atoms. The vacancy was introduced in such a way that an atom was substituted for with an empty sphere having the same radius as the corresponding atomic sphere. Assuming that the electron density in the vacancy sphere is caused mostly by the dangling bonds of the four surrounding atoms, for the vacancy sphere the value of the U_p -parameter was chosen to be equal to that of the surrounding atoms.

Unfortunately, within the version of the LMTO method used in the present work we could not optimize the atomic positions around a vacancy. The spherical approximation for the potential in the ASA as well as the changes in the overlapping of the atomic spheres, due to relaxation shifts, affect the calculation of the total energy, which cannot be accurate enough to locate the positions of the relaxed atoms. Therefore we have simulated relaxation shifts up to 15% of the interatomic distance and discuss their effects on the local electronic structure.

3. Local electronic structure around single vacancies

In silicon carbide crystals the electronic charge on Si–C bonds is shifted towards the carbon atom [2–4, 8]. Therefore a V_{Si} vacancy would behave as an acceptor whereas a V_{C} vacancy would behave as a donor [19, 20].

We start our considerations with the case of the local electronic structure around a vacancy in the case of the non-relaxed atomic surrounding. The four dangling bonds of the neighbouring atoms should create four electron states. The symmetry of these vacancy states corresponds to the a_1 (one-state) and t_2 (three-state) irreducible representations of the T_d point symmetry group. In the vacancy sphere the angular momentum expansion of the wave function provides only s contributions for the state of a_1 symmetry, and p contributions for the t_2 states. Furthermore, because of exclusively bonding character of the interaction between dangling bonds in the a_1 state, this state lies at lower energy than the t_2 states. These symmetry considerations give a qualitative picture of the electron states around the vacancy site and could be helpful for analysing the calculated results. In fact, the following considerations should also be taken into account. Due to the hybridization with the band states of the SiC crystal, the vacancy electron states could not be well separated as pure states of a_1 and t_2 symmetry (with the exception, perhaps, of localized split-off levels in the band gap), but they could be found as resonance states against the background of the band-like contributions in the vacancy sphere. The interaction with the band states can also cancel the threefold degeneracy of the t_2 states.

In figures 1 and 2 the calculated local DOS for the vacancy sphere and that for the surrounding atoms are presented. The vertical line in each figure indicates the valence band maximum for the perfect crystal, taken as the zero of energies. It can be seen that around the V_{Si} vacancy a localized electronic state in the band gap at the energy of 0.38 eV is created. This state is unoccupied and it is spatially distributed mostly in the spheres of the C atoms, which are the nearest neighbours of the vacant site, as well as in the vacancy sphere. Both this state and the occupied resonance state just at the top of the valence band ($E = -0.33$ eV) have dominating p character (t_2), and they are caused by carbon dangling bonds which would be 'saturated' by Si electron states in the perfect crystal. s states in the vacancy sphere (the a_1 contribution) could be observed as a peak at the energy of -1.5 eV. The energy distribution of the electron states in the valence band of the neighbouring carbon atoms is not significantly disturbed by the presence of the vacancy.

In the case of the V_C vacancy the Si dangling bonds produce the occupied split-off state in the band gap at the energy of 2.15 eV as well as the resonance state at the bottom of the conduction band ($E = 3.0$ eV). These states belong to the t_2 representation. We have also found a resonance peak at $E = -0.43$ eV, created by the electron states of s symmetry in the vacancy sphere (the a_1 contribution).

In order to study the effect of relaxation shifts of atoms on the energy positions of vacancy states, we have performed calculations for structures where the atoms nearest to the vacancy

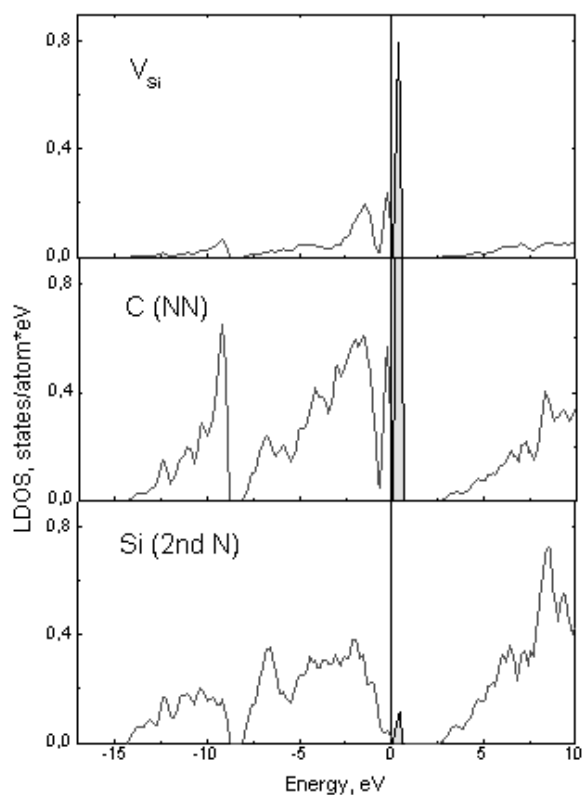


Figure 1. The calculated local densities of electron states for a V_{Si} vacancy site, for C-atom nearest neighbours of the vacancy (NN) and for Si atoms (second neighbours, '2nd N'). No lattice relaxation is taken into account. Shaded areas indicate the electron states in the energy gap.

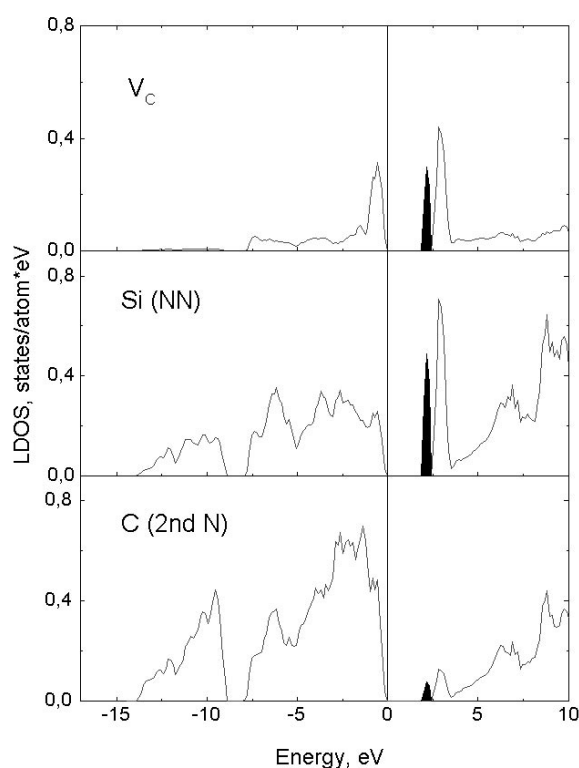


Figure 2. The calculated local densities of electron states for a V_C vacancy site, for Si-atom nearest neighbours of the vacancy (NN) and for C atoms (second neighbours). No lattice relaxation is taken into account. Shaded areas indicate the electron states in the energy gap.

were shifted outwards, retaining, however, the T_d symmetry around the vacancy. It can be seen from figure 3 that an outwards shift of the surrounding atoms moves the vacancy electron states to higher energies. At the same time there are clear differences between the behaviours of the V_{Si} states and V_C states. In the case of V_{Si} the energy shift of the split-off state is very small: atomic relaxation up to 15% changes its energy position from 0.38 eV to 0.50 eV. In contrast, just 5% relaxation around V_C increases the energy of the occupied split-off state so that it reaches the bottom of the conduction band. Further increasing the energy can lead to the occupation of the lowest band states and to the delocalization of the electronic charge which was initially related to the vacancy state. At the same time, the resonant a_1 state moves from the valence band to the gap. This behaviour of the vacancy states is easy to understand, if we take into account the fact that the 2p orbitals of carbon are more strongly localized on atoms than the 3p orbitals of silicon. Consequently, due to the weak interaction between dangling bonds of C atoms around V_{Si} vacancies, the energy position of the vacancy state is only slightly sensitive to the changes in the interatomic distances. A higher sensitivity of the V_C vacancy states to the shifts of atoms surrounding the vacancy could be evidence of a significant interaction between the dangling bonds of the Si atoms.

Ivashchenko *et al* [22] have obtained theoretically the same behaviour of the vacancy states caused by the outward shift of surrounding atoms. Some quantitative differences from our results could be explained, in our opinion, by the simplified approximations for the two-centre parameters which were chosen in [22]—depending as $\sim R^{-2}$ on the bond length R .

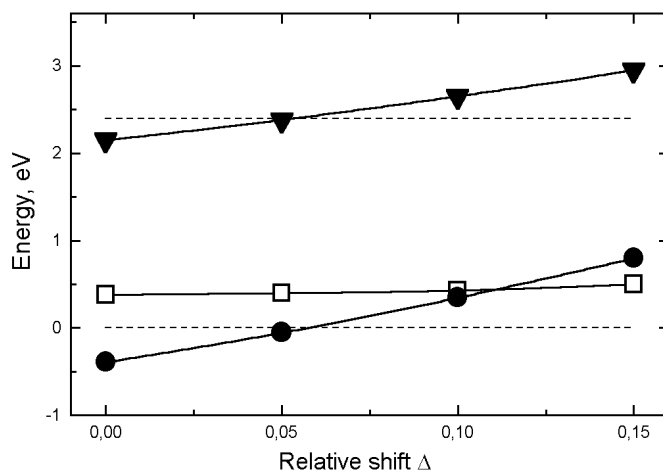


Figure 3. The dependence of the energy position of the vacancy levels on the local lattice relaxation. The values of the outwards atomic shift Δ are given in units of the interatomic Si–C distance in the perfect crystal. Open squares denote the t_2 level of the V_{Si} vacancy. For the V_C vacancy the positions of the a_1 level (solid circles) and the t_2 level (solid triangles) are shown.

Let us consider the distribution of the electronic charges in the atomic spheres. The partial compositions of the valence electronic charges for atoms surrounding the vacancies are given in table 1.

Table 1. Valence electronic charges in the ASA spheres for atoms surrounding a vacancy.

Valence charge	Perfect crystal	Nearest neighbour to vacancy			
		Non-relaxed	Relaxed 5%	Relaxed 10%	Relaxed 15%
C (total)	3.987	3.634	3.704	3.752	3.777
s	1.161	1.188	1.188	1.184	1.177
p	2.785	2.412	2.481	2.532	2.563
d	0.041	0.034	0.035	0.035	0.037
Si (total)	2.588	2.418	2.478	2.526	2.550
s	0.860	0.878	0.876	0.868	0.856
p	1.394	1.288	1.338	1.381	1.404
d	0.334	0.252	0.264	0.276	0.290

It can be seen that in all cases removing an atom from the lattice site leads to a decrease of the electronic charge in the atomic spheres of the nearest neighbours (as compared with the valence electronic charges for atoms in the perfect lattice). However, due to the polarized character of the Si–C bonding, this decrease is more significant at carbon atoms surrounding V_{Si} vacancies than for silicon atoms surrounding V_C vacancies. This fact can be understood if one considers that in the latter case the decreasing of the electronic charge is compensated to some extent by the charge which was shifted towards the carbon atom in making the Si–C bond and is returned to the Si atom after the bond has been broken.

In order to analyse the partial composition of the valence electronic charge we introduce the parameter

$$\gamma = \frac{n_p + n_d}{n_s}$$

characterizing the deviation of the electronic charge distribution from the spherical one. In the perfect β -SiC crystal this parameter has values of $\gamma = 2.01$ for Si atoms and $\gamma = 2.40$ for C atoms, indicating a stronger localization of the electronic charge along the bonds in the vicinity of the carbon atoms. It is also interesting to note that these values of γ are very close to those obtained from the results of calculations for the pure silicon crystal and for diamond [9].

Let us assume that at the atom in the perfect-lattice position the valence electronic charge is distributed in equal parts among four bonding orbitals, and that at one of the atoms surrounding the vacancy only one orbital is significantly perturbed by the presence of the vacancy, while the charge distribution along the other three bonds is unchanged. Then the contribution of the dangling bond could be calculated from the values given in table 1. For the non-relaxed case we obtain $n = 0.477$ ($n_s = 0.233$, $n_p = 0.243$, $n_d = 0.001$) for the Si atom at V_C and $n = 0.644$ ($n_s = 0.317$, $n_p = 0.323$, $n_d = 0.003$) for the C atom at V_{Si} . It can be seen that d contributions practically disappear. The values of γ are equal to 1.04 for Si atoms and 1.03 for C atoms. Note that the values for the two kinds of atom are very close, and they are also close to $\gamma = 1.0$, the value for the free Si and C atoms. For atoms shifted outwards from the vacancy the value of γ increases, indicating that electrons from dangling bonds are involved in interatomic interactions. However, as we have seen above, the changes in the local electronic structure around V_C and around V_{Si} are quite different.

The C atoms surrounding a V_{Si} vacancy no longer have the electronic charge which has been pulled out from the fourth Si atom in the perfect lattice. This loss is partly compensated after shortening the remaining three Si–C bonds, which become stronger. The dangling bond remains mostly localized on the carbon atom and makes only an insignificant contribution to the antibonding interaction. Thus, the outwards shift of the carbon atoms leads to the gain in binding energy, and this model of lattice relaxation around V_{Si} could be accepted.

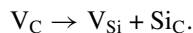
In contrast, the shortening of the Si–C bonds, due to the outwards shift of the Si atoms surrounding the V_C vacancy, is not advantageous. First, the perturbation of the stable four-bonded state of C atoms (second neighbours to the vacancy) would not give a gain in the binding energy, because the carbon orbitals are ‘saturated’ with electronic charge attracted from Si atoms and, second, the dangling-bond charge (which is significantly less localized than in the case of V_{Si}) is involved in antibonding interaction with the electronic charge of bonding orbitals. As a result, the vacancy level is strongly pushed upwards to higher energies. It seems that a more reliable model for lattice relaxation around V_C would have to assume the distortion of the tetrahedral arrangement of four Si atoms, with creation of two Si–Si bonds (four dangling bonds are closed in pairs) with decrease of the local symmetry around the vacancy ($T_d \rightarrow D_{2d}$). *Ab initio* pseudopotential calculations [24] predict D_{2d} symmetry for all carbon vacancies except negatively charged V_C^{2-} which is characterized by uniform outward shifts of the surrounding Si atoms. The carbon vacancy in β -SiC is found to be in a D_{2d} configuration also, from the experimental investigations [12].

4. Vacancy–antisite complexes

4.1. $V_{Si} + Si_C$

In the previous section the models for the local lattice relaxation around the single vacancy were discussed. If these models are accepted, the different behaviours of V_C and V_{Si} with increasing temperature could be explained. In fact, due to the Si–Si bonds created around a V_C vacancy, one of the Si atoms could be easily activated for hopping into the vacancy site. As a result, the carbon vacancy would decay into a vacancy–antisite complex (here we denote—as usual—the antisite defect due to a Si atom replacing a C atom as Si_C , and the antisite defect

due to a C atom replacing a Si atom as C_{Si}):



This could be one of the possible ways of annealing out the vacancy at temperatures above 200 °C. On the other hand, energy considerations show that the probability of this process seems to be very small. In fact, direct comparison of the formation energies for different point defects in β -SiC [19] gives

$$E(V_C) = 5.9 \text{ eV} \quad \text{and} \quad E(V_{Si}) + E(Si_C) = 6.8 + 7.3 = 14.1 \text{ eV}.$$

Since no reports of experimental observation of the $V_{Si} + Si_C$ complex have been published, one can assume this kind of defect to be unstable and to decay into two single defects.

We have performed the electronic structure calculations for the $V_{Si} + Si_C$ complex. In figure 4 the local DOS is presented for the case of atoms that are positioned at sites of the perfect lattice (no atomic relaxation). It can be seen that, as in the case of a single Si_C antisite [9], the local DOS in the Si_C sphere shows two resonances: an s-like resonance state at -8.85 eV and a p-like resonance state near the energy -1.0 eV . Due to the decreased local symmetry, as compared to that of the single antisite, the latter state is split into three peaks. Despite the fact that the main intensity of the p resonance lies at lower energies than in the case of

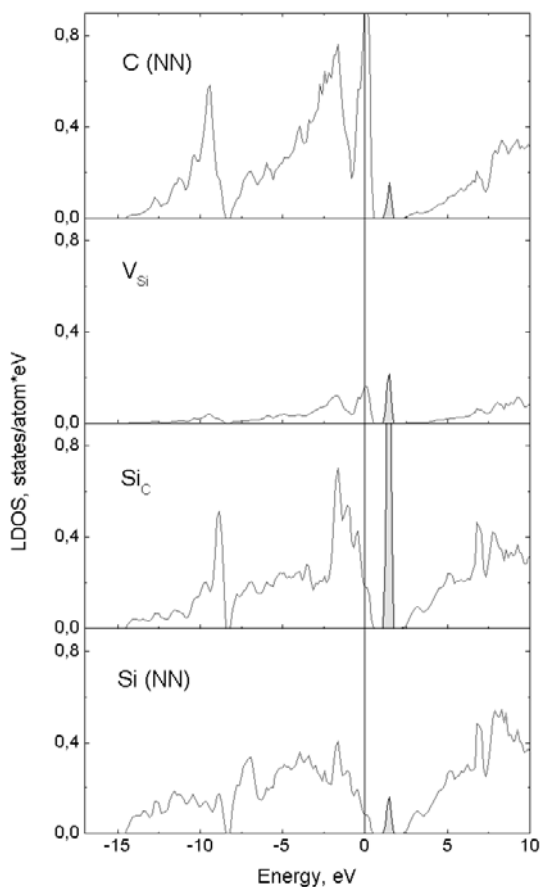


Figure 4. The local densities of electron states for the $V_{Si} + Si_C$ complex calculated without taking into account the lattice relaxation. Shaded areas indicate the electron states in the energy gap.

the single antisite, these Si p states still cause a small displacement of the valence band top towards higher energies. This is a characteristic feature for the appearance of the Si–Si bonds in non-perfect SiC crystals. By comparing the local DOS in the sphere of the carbon atom which is the nearest neighbour of the V_{Si} vacancy with that given in figure 1 for the case of a single vacancy, one can see that these pictures differ by the split-off vacancy state, which is not yet split from the valence band in the non-relaxed vacancy–antisite complex.

An especially interesting feature for the $V_{Si} + Si_C$ complex is the localized state in the energy gap at 1.45 eV. This unoccupied state is related to the dangling bond on the antisite silicon atom and should disappear in the single Si_C antisite if the vacancy–antisite complex decays into single defects. Thus, this level could be considered as a characteristic feature for the existence of the $V_{Si} + Si_C$ complex.

It should be noted that the electronic charge in the carbon atomic sphere adjacent to the V_{Si} vacancy ($n = 3.704$) is larger than that in the non-relaxed carbon atomic sphere at the single V_{Si} vacancy (see table 1). The electronic charge in the Si_C atomic sphere has the value $n = 2.907$, which is not as large as that for a single antisite [9] but exceeds, however, both the value for Si atoms in the perfect lattice and that for Si atoms surrounding a single vacancy. Thus, due to the displacement of electronic charge towards the atoms surrounding the vacancy, the V_{Si} vacancy in the vacancy–antisite complex has a lower electron density than the single V_{Si} vacancy. This could indicate a weak repulsive interaction between Si_C and carbon atoms surrounding the vacancy and, consequently, instability of the $V_{Si} + Si_C$ complex.

In order to study the effect of atomic relaxation on the local electronic structure we have performed the calculations assuming the following model for the relaxation shifts of the atoms: carbon atoms are shifted outwards from the vacancy (as in the case of the single V_{Si} vacancy) whereas the Si_C antisite is shifted towards the vacancy in order to lengthen the Si–Si bonds. In this case the centre of the vacancy sphere should also be placed off the perfect-lattice site (it is ‘pushed out’ by Si_C). The values of the atomic shifts were chosen equal to 10% of the interatomic distance in the perfect SiC crystal for carbon atoms and to 12% for Si_C [9]. These relaxation shifts affect qualitatively only the local DOS of the carbon atoms neighbouring the vacancy: the high peak at the top of the valence band is split and the split-off state in the energy gap is created. This energy distribution of the electron states is very close to that for the single V_{Si} vacancy (figure 1); however, in the vacancy–antisite complex the dangling-bond state is much more strongly localized on the carbon atom. This may be a result of the repulsive interaction with more extended Si_C electron states which are absent in the case of the single vacancy. The localized level at 1.45 eV is not very sensitive to the atomic relaxation: the displacement of atoms causes the upwards shift of this level, as well as of all the resonance states in the valence band of Si_C , by 0.3 eV.

4.2. $V_C + C_{Si}$

The V_{Si} vacancy is surrounded by carbon atoms strongly bonded to the silicon atoms which are second neighbours of the vacancy. This causes a high thermal stability of V_{Si} up to 700–750 °C. In [11] the defect in β -SiC, labelled as the $L2$ centre, was investigated and it was shown that it has T_d symmetry and begins to be annealed out at temperatures higher than 750 °C. This defect was interpreted as being related to a silicon vacancy. A new kind of defect in β -SiC, denoted as an $L3$ centre, was recently [13] reported. It appears after annealing at 750 °C; its signal decreases in intensity at higher annealing temperatures and disappears at 900 °C. It was found that this defect has a trigonal symmetry (it is symmetric along the $\langle 111 \rangle$ direction of the crystal) and it is related to a photoluminescence band in the near-midgap region.

It could be expected that at the specific temperature of 700–750 °C the carbon atoms would

be rearranged to create stronger C–C bonds:



The comparison of formation energies for point defects given in [19] shows that

$$E(V_{\text{Si}}) = 6.8 \text{ eV} \quad \text{and} \quad E(V_{\text{C}}) + E(C_{\text{Si}}) = 5.9 + 1.1 = 7.0 \text{ eV} > E(V_{\text{C}} + C_{\text{Si}}).$$

Thus, the probability for this process should be quite considerable.

We have calculated the local electronic structure of the $V_{\text{C}} + C_{\text{Si}}$ complex. The valence DOS are presented in figure 5. If we compare the local electron states in the V_{C} sphere with those obtained for the single carbon vacancy (figure 2), it could be concluded that the main features are displayed also for the vacancy–antisite complex: there are resonance states at the top of the valence band (s symmetry) and at the bottom of the conduction band (p symmetry), as well as the occupied split-off state in the gap (p symmetry). However, the resonance states are shifted by 0.2 eV to higher energies (as compared to their positions at the single vacancy), while the vacancy level in the gap has a significantly lower energy (1.55 eV). This electron state is spread out over the vacancy sphere as well as over four atomic spheres surrounding the vacancy. In the valence band of the C_{Si} antisite there are two resonance states at -7.6 eV

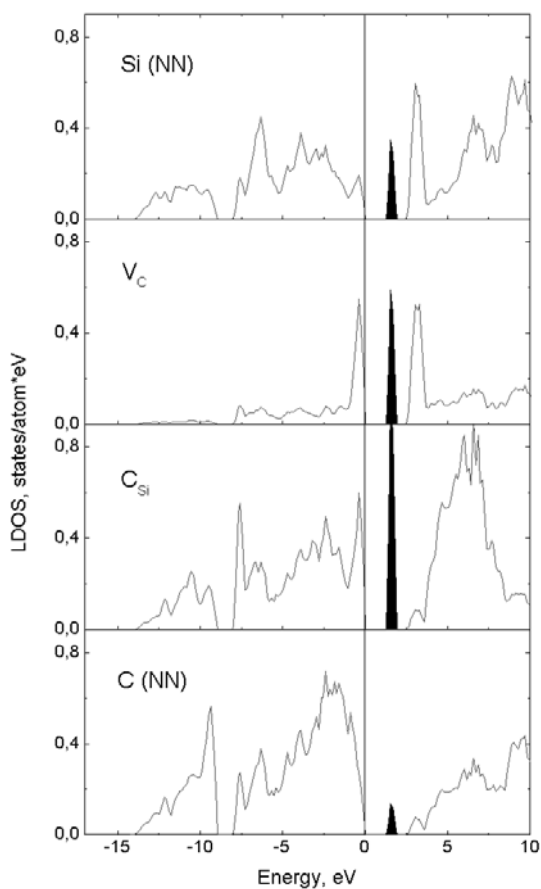


Figure 5. The local densities of electron states for the $V_{\text{C}} + C_{\text{Si}}$ complex calculated without taking into account the lattice relaxation. Shaded areas indicate the electron states in the energy gap.

(s symmetry) and at -0.22 eV (p symmetry). In contrast, with respect to the case of the single C_{Si} antisite [9], these resonances are at significantly higher energies and reflect (especially the p states at the top of the valence band) the interaction between C_{Si} and the three silicon atoms around the vacancy. From the a_1 symmetry of these states in the vacancy sphere an attractive character of this interaction can be concluded. This is suggested also by the more homogeneous spatial distribution of the electronic charge: in the silicon atomic sphere neighbouring the V_C vacancy it is equal to $n = 2.335$, smaller than in the silicon atomic sphere at the single V_C vacancy (see table 1). The electronic charge in the C_{Si} atomic sphere has the value $n = 3.280$, which is smaller than both that for a single antisite [9] and that for carbon atoms surrounding a single vacancy. Thus, after the carbon atom has moved from its *official* lattice site to the antisite position, the bonding to three silicon atoms is not broken.

As a model for the local atomic relaxation in the $V_C + C_{Si}$ complex, let us assume that the C_{Si} atom shifts towards the nearest carbon atoms in order to shorten the C–C bonds. Our calculations show that this shift, up to 10% of the perfect Si–C interatomic distance, destroys the C_{Si} –Si interaction, producing the decay of the vacancy–antisite complex. The resonance states in the valence band of C_{Si} disappear and the centre of gravity of the local DOS is shifted downwards, while an increasing of the DOS intensity is observed at energies characteristic of the resonance states in a single C_{Si} antisite. The vacancy split-off level moves towards higher energies and reaches the value obtained for the single V_C vacancy (see figure 2).

Another model could be suggested as follows: C–C bonds are shortened by shifts of the three carbon atoms nearest to the C_{Si} antisite, like in the case of the relaxation around a single C_{Si} antisite [9], and silicon atoms are shifted towards the vacancy (they ‘follow’ carbon atoms moving to the antisite position because of the strong bonding). In this case the split-off level is located in the middle region of the gap at an energy smaller than 1.55 eV and it is dependent on the shift of the Si atoms. The main condition for existence of this split-off state in the midgap region is the bonding interaction between Si and C_{Si} atoms. At the same time, this interaction is responsible for the stability of this kind of defect. Thus, it could be suggested as a possible explanation of the $L3$ centres observed in β -SiC [13]. Unfortunately, in our considerations we cannot predict the real positions of the silicon atoms. Due to the large number of atoms, displaced from their *official* sites, and due to the complicated bonding character (Si–Si, C–C as well as Si–C bonds), perhaps speaking of a vacancy–antisite complex would no longer make sense. It would be rather similar to the bond defect described in [33] for silicon crystal, as a result of incomplete recombination of a vacancy–interstitial pair.

5. Conclusions

In conclusion, by using an *ab initio* LMTO approach, we have computed the electronic structure of β -SiC containing vacancies and vacancy–antisite complexes. The main attention has been paid to the effects of the atomic relaxation around the defects on the local electronic structure of crystals. Different models for displacements of atoms around the defects are discussed. It has been shown that in β -SiC crystal the silicon vacancy creates an unoccupied localized split-off electron state in the gap above the top of the valence band, while the carbon vacancy is responsible for the occupied split-off state below the bottom of the conduction band. The outwards shift of the atoms surrounding the vacancy moves the localized vacancy states to higher energies. The energy position of the split-off electron state in the V_{Si} vacancy is only slightly influenced by the relaxation shifts of the carbon atoms. In contrast, the localized electron state related to the V_C vacancy is very sensitive to the outwards shift of the surrounding Si atoms. This could be evidence for a significant interaction between the dangling bonds of Si atoms. Study of the local electronic structure around V_C shows that the outwards relaxation of

Si atoms is not advantageous. The more reliable model is that of the distortion of the tetrahedral arrangement of four Si atoms with creation of two Si–Si bonds [24].

The calculations of the local electronic structure performed for the vacancy–antisite complexes show that the $V_{Si} + Si_C$ complex is characterized by a repulsive interaction between a Si_C antisite and three carbon atoms surrounding the vacancy, and it should be unstable. The stability of the $V_C + C_{Si}$ complex is also determined by the interaction of the atoms surrounding the vacancy. For the non-relaxed positions of the atoms the bonding between C_{Si} and Si atoms stabilizes this complex. However, the real behaviour of this defect is dependent on the rearrangement of atoms due to the relaxation process. In all cases the appearance of the localized electron state in the middle region of the energy gap is a characteristic feature of the vacancy–antisite complex, and this could be used in experimental confirmation of the existence of these complexes.

On the basis of the results of our calculations we propose some possible mechanisms of the annealing out of the vacancies in β -SiC. The decay of the V_C vacancy into a V_{Si} vacancy and Si_C antisite seems to be not very probable due to the energy balance. Another possibility is the interaction of the V_C vacancies with C_{Si} antisites which have low formation energy (1.1 eV [19]) and should exist in SiC crystal at 200 °C. As a result of this interaction, V_{Si} vacancies are created (the process opposite to that considered in subsection 4.2). The V_{Si} vacancy, which is stable up to 750 °C, could decay with the creation of a vacancy–antisite complex $V_C + C_{Si}$ (which is substantially distorted by the local atomic relaxation) that has a high stability and could exist up to 900 °C. Certainly, further experimental and theoretical investigations are necessary in order to confirm the proposed models for the processes of the annealing out of the vacancies in β -SiC.

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