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Deep gap states of a single vacancy in cubic SiC

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Abstract. The character of relaxation of atoms around a vacancy in cubic silicon carbide is determined with the help of the empirical potential of Tersoff. The recursion method of Haydock and Nex is applied to calculate the density of states derived from atoms situated around the defect. The outward relaxation of the lattice surrounding a empty site is established. The lattice relaxation results in the shift of gap states toward the conduction band. Vacancy levels of carbon at 0.5 eV and silicon at 0.45 and 1.98 eV are revealed in the band gap. The obtained results are compared with the experimental ones and with the data of other calculations. The work shows the importance of taking into account the lattice relaxation in examining vacancy states in semiconducting compounds.

1. Introduction

The influence of point defects on the electronic structure and properties of materials is sharply exhibited in semiconductors [1–3]. As it is known, the most widely distributed point defects in crystalline semiconductors are vacancies, antisites, hydrogen–vacancy complexes, substitutional and interstitial atoms. The creation of a point defect is accompanied by the relaxation of the lattice surrounding this defect. In this work we are concerned with a vacancy in crystalline cubic silicon carbide (3C-SiC).

Lattice vacancies can be created in semiconductors by electron or neutron irradiation [4]. Most vacancies are thermally quite stable; in particular, in 3C-SiC vacancies do not anneal out below 750 °C [5]. The electronic structure of vacancies can be understood within the one-electron orbital model [2, 6]. The removal of a atom from the lattice introduces four dangling bonds at the position of the four ligands next to the vacancy. For an undistorted vacancy in a cubic crystal, the symmetrized dangling-bond orbitals transform according to the a_1 and t_2 irreducible representations of the T_d group, respectively. As a rule, the a_1 state forms a resonance in the valence band (resonance state, RS). In contrast, the t_2 state gives rise to a gap state (GS). These states in 3C-SiC were carefully studied by experimental [7, 8] and theoretical methods [9–13]. In particular, Nagesh *et al* [7], using deep-level transient spectroscopy (DLTS), in chemical vapour deposition grown 3C-SiC films did not observe deep levels due to native defects. In contrast, the DTLS measurements of Zhou *et al* [8] have suggested the occurrence of two deep states (near 0.34 and 0.68 eV) below the bottom of the conduction band.

Recently, there has been a number of theoretical studies of vacancy states in 3C-SiC [9–13]. Using the recursion method of Haydock and involving the set of semiempirical two-centre integrals, Yuan Li and Lin-Chung [9] have found that C and Si vacancies will behave as acceptors and donors, respectively. However, Wang *et al* [10] on the basis of supercell pseudopotential calculations have found the opposite behaviour, i.e. that C and Si vacancies

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have to act as donors and acceptors, respectively. Talwar and Feng [11], using the Green function (GF) method within the tight-binding (TB) approximation, and Wenchang *et al* [12], using the GF matrix technique based on the LMTO method within the atomic sphere approximation, have observed the same behaviour as Wang *et al* [10]. Deep gap levels derived from Si and C atoms surrounding the vacancy have been studied by Robertson [13] in the framework of the recursion method with the use of the set of the first-neighbour (FN) TB parameters including those connected with the additional high-energy s state. The latter is necessary to reproduce correctly the indirect band gap in 3C-SiC. The mentioned calculations have been carried out without taking into account the relaxation of the lattice surrounding a vacancy.

The character of the relaxation of atoms around a vacancy has been investigated by Hanchen Huang and Nasr Chonien [14] on the base of the molecular dynamics calculations, using empirical potentials. They have only found that atoms surrounding a vacancy relax towards the vacancy (as in the case of Si [15] and C [16]) and that the relaxation of the lattice around the Si vacancy was considerably larger than that around the C vacancy.

In this paper we present the results of the investigation of the density of states (DOS) derived from atoms surrounding a vacancy. For investigating the relaxation of the lattice around a vacancy we have used the empirical potential of Tersoff [17]. The electronic structure of the defect has been investigated by the recursion method of Haydock *et al* [18] and Nex [19] within the framework of the TB approximation [20].

2. Computational aspects

Recently, the Tersoff potential has been successfully used for the investigation of the chemical order in amorphous silicon carbide [21], for describing C defects in Si [22]. By studying the molecular C–Si–H complexes a version of this potential has been applied by Beardmore and Smith [23].

In the Tersoff formalism the potential energy is written as a sum over pairs

$$
\begin{aligned}
V &= 1/2 \sum V_{ij} \\
V_{ij} &= f_c(r_{ij})[f_R(r_{ij}) + b_{ij} f_A(r_{ij})] \\
f_R(r) &= A \exp(-\lambda_1 r) \\
f_A(r) &= B \exp(-\lambda_2 r)
\end{aligned}
\qquad (1)
$$

where f_R and f_A are pair repulsion and attraction terms respectively, r_{ij} is the bond length between atoms i and j, b_{ij} is a many-body function and f_c is a cutoff function limiting the range of the potential between only first neighbours. Details of terms in (1) can be found elsewhere [17, 22]. The parameters of this scheme for 3C-SiC have been taken from the work [17]. The coordinates of the relaxed crystal of 3C-SiC have been obtained using the Tersoff potential by means of the conjugate-gradient method.

For carrying out the calculations in the framework of the recursion method it is necessary to introduce the parameters of the LCAO interpolation scheme of Koster and Slater [20]. We have used the basis of four Si and C orbitals (one s and three p) which have been taken as orthonormal. To determine the transfer integrals we have parametrized the dispersion curves [24]. This fitting has been performed using eigenvalues of the valence band and of the lowest conduction band. We have used the eigenvalues at the symmetry points Γ, X, L and K in the Brillouin zone. The LCAO parameters are expressed in terms of the two-centre integrals which include the first- and second-neighbour (SN) interactions. The root-mean-square deviation in our LCAO fits was 0.2 eV. The two-centre LCAO parameters for 3C-SiC defined in such a way

Table 1. The parameters of the LCAO interpolation scheme (in eV). The notations are those of Koster and Slater [20]. The bond length R_0 (in Å).

	Si–C	Si–Si	C–C
E_s		−4.868	−8.832
E_p		2.063	0.250
ssσ	−3.109	0.310	−0.304
spσ	2.786	0.000	0.000
psσ	−3.571	0.000	0.000
ppσ	3.319	0.741	0.552
ppπ	−0.487	−0.121	−0.006
R_0	1.888	3.083	3.083

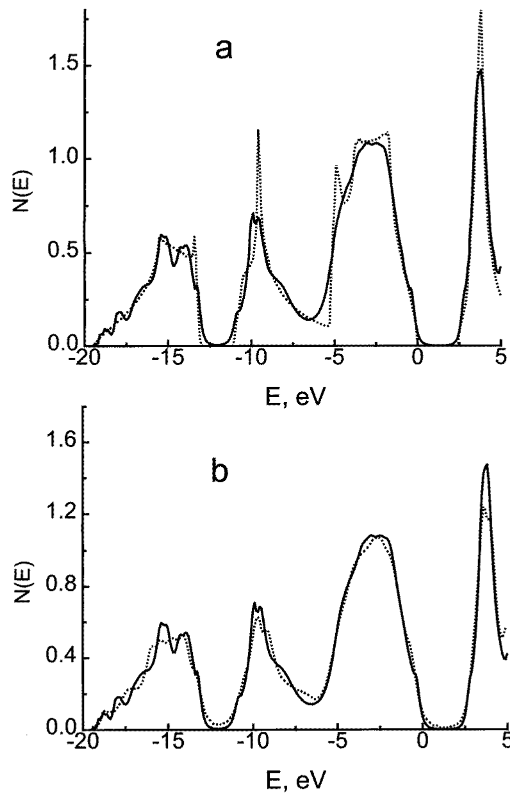

Figure 1. The DOS of 3C-SiC determined by the different methods: (a) the RM, NA = 1728, NRC = 30 (full line) and the tetrahedron method (dashed line); (b) the RM, NA = 1728, NRC = 30 (full line) and the RM NA = 1000, NRC = 20 (dashed line). The energy gap is in the region of 0.0–2.4 eV.

are listed in table 1. In calculating the DOS of the relaxed crystal the two-centre parameters have been changed in the dependence on bond lengths (R) as R^{-2}, according to the Harrison rule [25].

In the present investigation the DOS of silicon carbide have been calculated on the basis of the recursion coefficients by the method of Nex [21]. So far, for constructing the DOS of semiconductors the terminator procedure has been applied. Robertson [13] has concluded that

for archiving the acceptable accuracy it is necessary to take into account up to 43 recursion coefficients for a cluster of 4000 atoms. The method of Nex does not have such a shortcoming. We have used 20 and 30 coefficients in the clusters of 1000 and 1728 atoms respectively. We have calculated also the DOS by the tetrahedron method by using eigenvalues determined at 16 384 points in the full Brillouin zone with the help of the interpolation scheme. The DOSs obtained by different methods are shown in figure 1. One can see that the Nex method of constructing the DOS reproduces well the spectrum obtained by the tetrahedron method and is insensitive to changing the number of recursion coefficients (NRC) and of atoms in the cluster (NA). We have used the optimum parameters: NRC = 30 and NA = 1728. For these parameters the recursion DOS agrees quite well with the tetrahedron spectrum. We have also found that the method of Nex is less sensitive to boundary conditions than the termination method. Nevertheless, for increasing the accuracy we have introduced the periodic boundary conditions and therefore have avoided the influence of cluster surfaces on the bulk DOS. The method of Nex uses the integrated DOS, which is derived from the recursion coefficients. The final DOS is defined by means of an analytic differentiation of the integrated DOS. Since the latter does not have a thin structure, the final DOS will be smooth. In our approach, the electronic spectra have been calculated for each orbitals belonging to the atoms in the first and second coordination spheres with a centre at an empty site. The top of the valence band is taken as the origin of energies. All spectra are expressed in arbitrary units. In such an approximation the vacancy is expected to be neutral.

3. Results and discussion

As a result of the minimization of the functional V (1) for the single vacancy in the cluster of 1728 atoms we have obtained the following.

- C atoms in the first coordination sphere with the centre at an empty site shift symmetrically outwards by 20% and Si atoms in the second coordination sphere shift outwards by 0.7% (Si vacancy).
- A symmetric outward relaxation of the nearest neighbour Si atoms of 6% and of the next nearest neighbour C atoms of 0.3% are predicted (C vacancy).

Due to the lack of theoretical and experimental data about the relaxation of the lattice around a vacancy in 3C-SiC it is useful to compare these results with analogous data for Si [15] and C [16]. According to these data atoms situated around a vacancy shift outwards by 5% in Si and by 13% in C. Thus, from the comparison with these data one can see that, in the case of 3C-SiC, for an Si vacancy we have obtained larger relaxation in comparison with the one in diamond [16]. We hope that our results will stimulate further investigations to clarify the value of the relaxation of the lattice around a vacancy in silicon carbide.

In figure 2 the spectra of the relaxed crystal having a single vacancy, decomposed by site (the local DOS connected with Si and C atoms situated around a vacancy in the first and second coordination spheres) are presented. From figure 2 one can see that the DOS of the SN atoms of the vacancy changes insignificantly in comparison with the spectrum of the perfect crystal. Consequently, vacancy deep levels are mainly formed from electronic states belonging to atoms situated directly around the vacancy. The results presented in figure 2 show also that the creation of the single vacancy and the lattice relaxation result in the appearance of additional localized states in the band gap at 0.50 eV for the Si vacancy and at 0.45 and 1.98 eV for the C vacancy. Vacancy states are located in the energy gap in the form of the sharp localized peaks. It has been shown [2] that t_2 states have larger energy than a_1 ones. From this fact we conclude that, in the case of the Si vacancy, the a_1 states are RS and the narrow

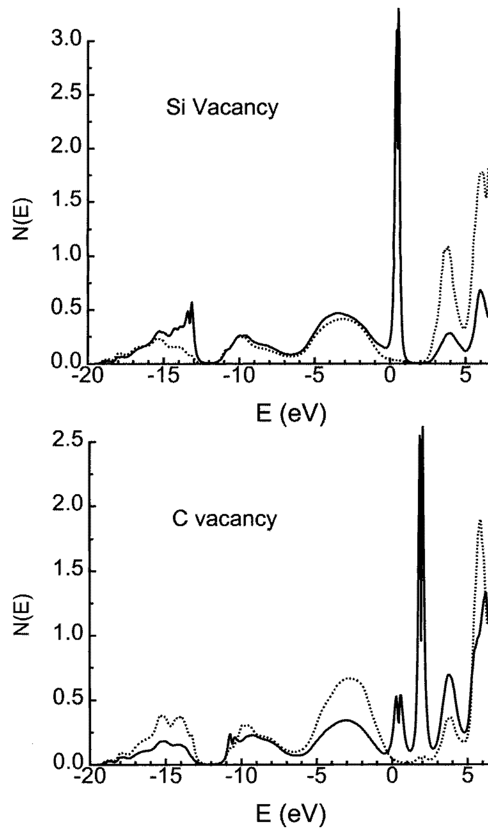

Figure 2. The DOS of nearest-neighbour atoms (full line) and of second-nearest-neighbour atoms (dashed line) surrounding the vacancy.

Table 2. The comparison of energetic positions of deep levels in the band gap of 3C-SiC obtained by the different methods. Vacancy levels are measured relative to the top of the valence band (in eV).

							Present work	
		[8][a]	[9]	[11]	[12]	[13]	Relaxed crystal	Unrelaxed crystal
Si	a_1		—	—	—	0.60	—	—
Vacancy	t_2		1.69	0.54	0.45	0.60	0.04	0.50
		1.72, 2.06						
C	a_1		—	—	—	2.00	0.12	0.45
Vacancy	t_2		0.54	1.66	1.67	2.00	1.76	1.98

[a] The experimental work, in which the symmetry of vacancy levels has not been determined.

level in the band gap can be connected with the t_2 dangling-bond states. For the C vacancy, two energetic levels with a_1 and t_2 symmetry are located in the band gap. Thus, the C vacancy generates two deep levels, deriving from Si states and the Si vacancy gives rise to the single GS derived from carbon states. These results show that Si vacancies will behave as acceptors and C vacancies will behave as donors and also as acceptors.

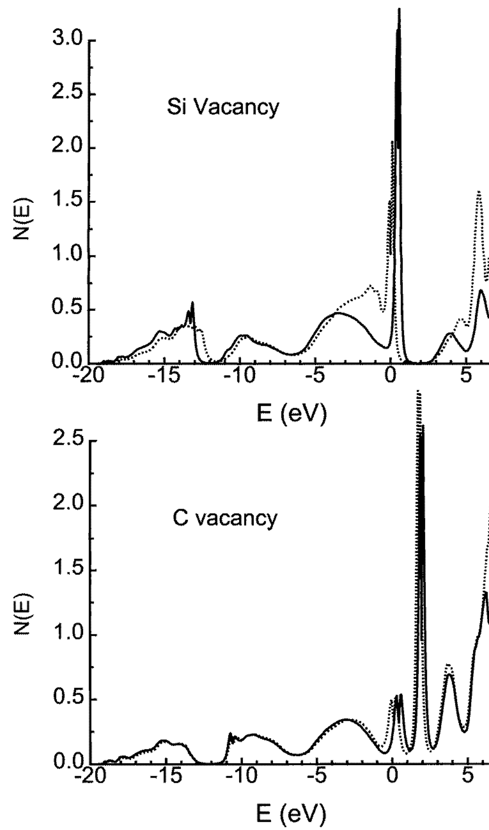

Figure 3. The comparison of the DOS of nearest-neighbour atoms surrounding the non-disturbed vacancy (dashed line) and the disturbed vacancy (full line).

To clarify the influence of the lattice relaxation on the electronic spectrum we have compared the DOS of the relaxed and unrelaxed crystals. The results of the comparison are presented in figure 3 and in table 2. (The latter contains also the energetic positions of vacancy gap levels in 3C-SiC obtained in the different works without taking into account the lattice distortion.) The relaxation turned out to result in the shift of deep levels toward the conduction band and the broadening of the valence and conduction bands. In the case of the Si vacancy, due to the large distortion of the lattice around the empty site, the shift of the gap levels is larger than those in the case of the C vacancy (table 2). From figure 3 one can see also that the relaxation of C atoms considerably modifies the bands derived from these atoms. Here it is worth pointing out that the described changes are similar to those revealed in the framework of the SN-TB model for GaAs and GaP by Ling-Chung and Reinecke [26] and Bernholc *et al* [27]. Allan *et al* [28] using the FN-TB-lattice Bethe model have also shown that, in the silicon crystal containing a single vacancy, the relaxation makes the single vacancy level move toward high energies. Taking into account these data one can conclude that the changes induced by the uniform outward lattice relaxation have general features and are independent of the nature of a semiconductor. In order to verify this statement and to study the influence of the lattice relaxation on vacancy states in the FN-TB approximation we have calculated these states in diamond. It was shown [29] that the FN-TB method well reproduces the energy

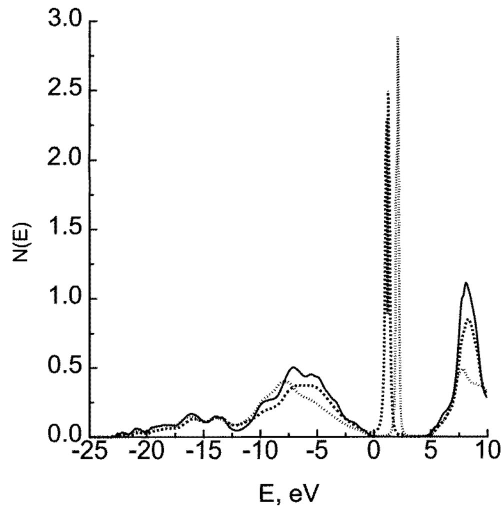

Figure 4. The DOS of atoms surrounding the vacancy in the unrelaxed (dashed line) and relaxed by 20% (dotted line) diamond crystals. The DOS of the perfect crystal (full line).

band of semiconductors having the direct band gap. Almost the same situation takes place in diamond. Therefore just carbon was chosen for investigation. Silicon carbide has an indirect gap equal to 2.4 eV [24] and therefore the FN-TB model is not suitable for studying energy bands in this compound.

In figure 4 we show the DOS of the unrelaxed and relaxed diamond crystals containing a single vacancy. The conditions of calculations are the same as for silicon carbide, except that the SN interactions have been neglected. The two-centre parameters have been taken from the work [30]. Figure 1 displays that the FN-TB method gives only the one vacancy level at 1.2 eV, which under the action of the lattice uniform outward deformation shifts to the conduction band. The GS position is 1.5 and 2.1 eV for the deformations of 6% and 20% respectively. So, the effect of the lattice distortion around a vacancy on electronic states is the same for the different types of semiconductor and is independent of the manner of the approximation of the transfer integrals in the TB model.

From table 2 one can see that our results are consistent with the experimental data (our GSs at 1.98 eV are close to ones at 2.06 eV revealed in the experiment) and with the theoretical ones [11–13]. But there exists an important difference. For the C vacancy we have obtained two deep levels. These levels have a_1 and t_2 symmetry. Here, it should be noted that an analogous result has been obtained for an anion vacancy in GaAs, AlAs [26] and GaP, InP [31]. Therefore, we assume that in semiconducting compounds the creation of anion vacancies and the further lattice relaxation have to result in the appearance of a_1 and t_2 GSs derived from cation atoms. We think that a_1 GSs have not been revealed in the work [9–12] because of the neglect of the relaxation effects. As earlier mentioned, the relaxation makes the a_1 and t_2 levels shift toward the conduction band. Consequently, if the RS is situated at the top of the valence band, the lattice distortion can shift it to the band gap. In our case, for the unrelaxed silicon carbide the C vacancy already gives a_1 and t_2 GSs, and the Si vacancy gives rise to an a_1 RS and t_2 GS. The a_1 states could not be obtained in the work [13] also due to neglecting the SN interactions. But, it is well known [2, 29] that one cannot obtain the split of a vacancy level considering only the FN interactions. This fact is confirmed by the results presented in figure 4. Yuan Li and Lin-Chung [9] have established that, in 3C-SiC, Si and C will behave as anion and cation

respectively. This contradicts the results of other theoretical investigations. But their result is true if one considers only the anion and cation GSs without their identification. Such a situation has arisen due to using incorrect TB parameters. Therefore it is very important to use the correct set of TB parameters in determining the position of GSs. The latter is confirmed also by the results of table 2 and the data of the investigations [26, 29–31].

4. Conclusion

Using the recursion method of Haydock and Nex we have performed realistic calculations of the DOS for 3C-SiC crystals containing a single vacancy in the unrelaxed and relaxed crystals. It was found that the creation of a vacancy results in the relaxation of atoms around a defect outwards; moreover, C atoms shift more than Si ones. In the band gap of the unrelaxed crystal, C vacancies give rise to a_1 and t_2 states and Si vacancies cause the appearance of t_2 states only. The uniform outward relaxation results in the shift of the vacancy levels toward the conduction band. We assume that in other semiconducting compounds anion vacancies have to generate two deep levels in the band gap too. This work stresses the importance of taking into account the relaxation effects in studying electronic states in the silicon–carbon crystal containing vacancies.

References

[1] Wertheim G K, Hausmann A and Sander W 1971 *The Electronic Structure of Point Defects* (Amsterdam: North-Holland)
[2] Lannoo M L and Bourgoin J 1981 *Points Defects in Semiconductors I (Solid-State Science 22)* (Berlin: Springer)
[3] Pantelides S T 1978 *Rev. Mod. Phys.* **50** 797
[4] Isoya J, Kanda H, Uchida Y, Lavson S C, Ymasaki S, Itoh H and Morita Y 1992 *Phys. Rev.* B **45** 1436
[5] Itoh H, Nayakawa N, Nashiyama I and Sakuma E 1989 *J. Appl. Phys.* **66** 4529
[6] Watkins G 1986 *Deep Centers in Semiconductors* ed S T Pantelides (New York: Gordon and Breach) p 1
[7] Nagesh V, Farmer J, Davis R F and Kong H S 1987 *Appl. Phys. Lett.* **50** 1138
[8] Zhou P, Spencer M G, Harris G L and Fekade K 1987 *Appl. Phys. Lett.* **50** 1384
[9] Yuan Li and Lin-Chung P J 1987 *Phys. Rev.* B **36** 1130
[10] Wang C, Bernholc J and Davis R F 1988 *Phys. Rev.* B **38** 12 752
[11] Talwar D N and Feng Z C 1991 *Phys. Rev.* B **44** 3191
[12] Lu Wenchang, Zhang Kaiming and Xie Xide 1993 *J. Phys.: Condens. Matter* **5** 891
[13] Robertson B J 1992 *Phil. Mag.* **66** 615
[14] Huang Hanchen and Nasr Chonien 1994 *J Nucl. Mater.* **212–215** 148
[15] Scheffer M, Vigneron J P and Bachelet G B 1985 *Phys. Rev.* B **31** 6541
[16] Messmer R P and Watkins G D 1973 *Phys. Rev.* B **7** 2568
[17] Tersoff J 1989 *Phys. Rev.* B **39** 5566
[18] Haydock R, Heine V and Kelly M J 1972 *J. Phys. C: Solid State Phys.* **5** 2845
[19] Nex C M M 1984 *Comput. Phys. Commun.* **34** 101
[20] Koster G F and Slater J C 1954 *Phys. Rev.* **95** 1167
[21] Tersoff J 1994 *Phys. Rev.* B **49** 16 349
[22] Tersoff J 1990 *Phys. Rev. Lett.* **64** 1757
[23] Beardmore B K and Smith R 1996 *Phil. Mag.* **74** 1439
[24] Hemstreet L A and Fong C Y 1971 *Solid State Commun.* **9** 643
[25] Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Francisco: Freeman)
[26] Lin-Chung P J and Reinecke T L 1983 *Phys. Rev.* B **27** 1101
[27] Bernholc J, Lipari N O, Pantelides S T and Scheffler M 1981 *Proc. 11th Int. Conf. on Defects and Radiation Effects in Semiconductors (Ocio 1980)* ed B R Hasiguti (Bristol: Institute of Physics) p 1
[28] Allan D C, Joannopoulos J D and Polard W B 1982 *Phys. Rev.* B **25** 1065
[29] Kauffer E, Pecheur P and Gerl M 1976 *J. Phys. C: Solid State Phys.* **9** 2319
[30] Winn M D, Rassinger M and Hafner J 1997 *Phys. Rev.* B **55** 5364
[31] Strivastava G P 1979 *Phys. Status Solidi* b **93** 761