Boron-vacancy complex in SiC

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First principle calculations have been carried out to investigate the position of a boron atom in a divacancy of cubic silicon carbide. The perfect lattice was modeled by a large molecular cluster. The total energy of the cluster was calculated within the local density approximation of the density functional theory and the wave function was expanded by linear combination of Gaussian type atomic orbitals. The results of the calculations on the boron-vacancy system resolve the contradiction between magnetic resonance and photoluminescence experiments regarding the deep boron center, establishing the $B_{Si}+V_C$ configuration as its origin.
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Silicon carbide (SiC) is a wide band-gap semiconductor material that has considerable potential for high-temperature, high-power, and high-frequency electronic applications. Boron is used as an important *p*-type dopant in SiC. It was discovered that B creates a shallow as well as a deep acceptor level.[1–5] The deep B center was then examined by photoluminescence measurements (PL).[4,6] Deep level transient spectroscopy (DLTS)[5,7] and capacitance methods[8] also point to the presence of a deep and a shallow boron acceptor level in 6H-SiC. The deep energy levels were estimated to be between $E_v+0.55$ eV and $E_v+0.75$ eV. These data have been confirmed by PL measurements in 4H-SiC[9] yielding $0.63+E_x$ eV, where E_x is the binding energy of the free exciton in 4H-SiC.

Analysis of the result of different measurement techniques showed that the shallow B-related acceptor level corresponds to an off-center boron substituting for a Si atom (B_{Si}).[10–12] This assignment was also supported by calculations.[13,14] In 6H material, the deep acceptor has recently been identified with a B atom on a Si site next to a C vacancy ($B_{Si}+V_C$) with axial symmetry parallel to the crystal *c* axis in electron spin resonance (EPR) and electron nuclear double resonance (ENDOR) experiments.[15,16] Duijn-Arnold *et al.*[16] have shown that the spin density of the singly occupied orbital in the neutral charge state of the center is negligible on the boron atom and about 70–90 % of it is localized on the three silicon atoms around the carbon vacancy. No significant difference was found between the $k_{1,2}$ and *h* sites, although the corresponding signals have been resolved.

Samples codoped with N and B have shown a Type I PL spectrum for the deep B acceptors recombining with the shallow nitrogen donors in 3C-SiC,[6] indicating that the ionized donor and acceptor occupy the same sublattice. Since the donor state is localized on N_C, the deep B center was associated with a complex containing B at a C site.[6] This is in clear contradiction with the ENDOR results above, which show B on the Si site.

An explanation for the contradicting PL and EPR/ENDOR results could be a possible bistability of the complex of a boron atom in a divacancy.[15,16] In the neutral charge state, seen in EPR, the configuration could be $(B_{Si}+V_C)^0$. In the negative charge state, observed in PL this could change to $(V_{Si}+B_C)^-$.

In this paper we will show by means of first principles calculations that the $(B_{Si}+V_C)$ configuration found in ENDOR is the relevant structure also in the negatively charged state but the charge is strongly localized on the Si neighbors of the V_C. This means that the V_C side of the complex acts as an acceptor. Since V_C is in the same sublattice as the N_C donor, this explains the Type I PL spectrum.

Ab initio calculations were performed using the local-density-functional[17] cluster method AIMPRO.[18] Ceperley-Alder[19] exchange-correlation and BHS norm-conserving pseudopotentials[20] have been applied. The total energy of the configurations with odd number of electrons were determined with spin-polarized calculations. The one-electron wave functions were expanded on a Gaussian type basis (GTO-*s*). For silicon and carbon eight *s*-type and eight *p*-type Gaussians were used, three *s*+three *p* and four *s*+four *p* GTO-*s* were taken for hydrogen and boron, respectively. For each bond between atoms of the first two shells around the defect, additional three *s*-type Gaussians were placed into the center of the bonds. (These bond center functions simulate the effect of *d* and *f* polarization functions.) The exponents of the Gaussians are preoptimized,[18] while the coefficients are independently varied in the SCF procedure of each calculation (no contraction to atomic orbitals). Earlier calculations showed that this method reliably provides structure, energies and vibrational modes of defect complexes in Si, diamond, SiC and GaAs.[21–26] In our calculations the perfect crystal is represented by a hydrogen-terminated $C_{31}Si_{40}H_{60}$ cluster. This cluster models cubic (3C) silicon carbide with T_d symmetry. (The environment of the central atom is identical with that of the *k* sites in hexagonal polytypes up to the second neighbor shell. In 4H and 6H, one atom of the third neighbor shell, lying on the *c* axis, is only 2% farther from the center than the second neighbors, though.) Considering the energy differences found between the investigated configurations and the results of recent con-

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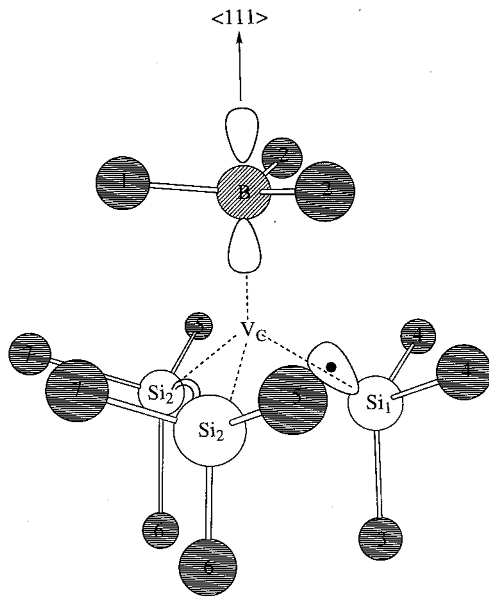

FIG. 1. The relaxed $(B_{Si}+V_C)$ complex in SiC (the circles with horizontal lines are the carbon atoms). Numbering refers to symmetry equivalent sites in the two sublattices. The electronic structure is shown in terms of localized orbitals (normal, long and dangling bonds as well as lone pairs). Occupation of the dangling bonds is also marked.

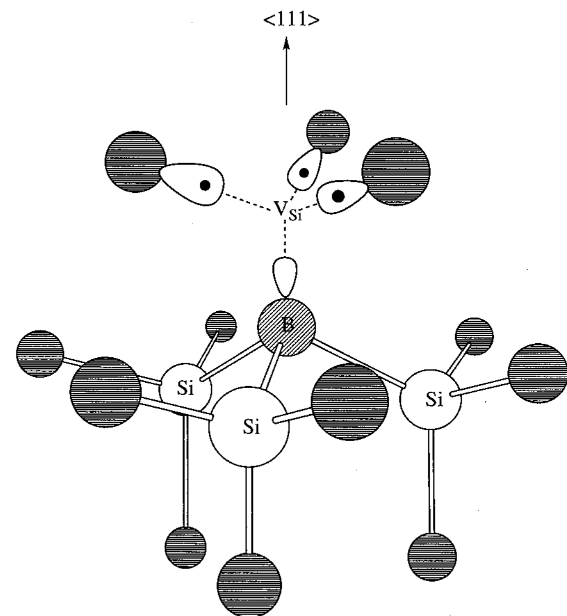

FIG. 2. The relaxed (B_C+V_{Si}) complex in SiC (for explanation see the caption of Fig. 1). The three singly occupied Si dangling bonds signify the absence of a notable Jahn-Teller distortion.

vergence tests on cluster size[27–29] our model turns out to be adequate for the problem. The carbon and silicon atoms were placed in perfect lattice sites known from experiment. The length of the terminating Si—H and C—H bonds have been tuned to give the most homogeneous charge distribution for both sublattices and no hydrogen related levels around the ''gap'' of the perfect cluster. The difference in Mulliken charge is within $\pm 0.1e$ for all relaxing Si and C atoms. The defect investigated is a divacancy in which the boron atom alternatively occupies the C or the Si site. The equilibrium structure of the defect has been determined by fixing the terminating pseudohydrogen atoms and the host atoms bonded to them, while allowing the rest of the atoms to relax.

Relaxing the cluster with the boron atom placed initially on the Si site of the divacancy results in the $(B_{Si}+V_C)$ configuration shown in Fig. 1. Starting the calculation (in the same cluster) with the boron initially placed on the C site gives rise to the $(V_{Si}+B_C)$ configuration depicted in Fig. 2. By comparing the calculated total energies for the relaxed geometries, the $B_{Si}+V_C$ complex turns out to be more stable by 3.78 eV in the neutral and by 2.22 eV in the negatively charged state than the $V_{Si}+B_C$ configuration. The difference is caused mainly by the fact that the B—C bond is stronger than the B—Si bond (an indication for that is given by the experimental dissociation energies of the corresponding diatomic molecules: B—C 4.6 and B—Si 3.0 eV), but also V_C is somewhat more stable than V_{Si}.[28] Based on the substantial energy difference in favor of the $B_{Si}+V_C$ configuration in both charge states, bistability can safely be excluded.

The symmetry of the unrelaxed B-V configurations is C_{3v}, giving rise to a fully occupied a_1 and an e defect level with only one (two) electron(s) in the neutral (negatively charged) state (see Fig. 3). The former falls into the valence band, the latter into the gap. This system is Jahn-Teller unstable; therefore, the calculated symmetry after relaxation is C_{1h} in both configurations for both charge states. (The geometry changes little between the two charge states of the same configuration.) The Jahn-Teller reconstruction splits the e level into an a_1' and a_2' level. The former is singly occupied, lies close to the valence band edge, and serves as an acceptor level. The electron distribution of $(B_{Si}+V_C)$ in the neutral charge state was analyzed by means of Mulliken-analysis.[30] For the acceptor level, 0.6, 68.3, and 0.5 % of the spin density is localized on the B atom, the three Si atoms around the vacancy, and on the carbon neighbors of boron, respectively. Two of the Si atoms move closer and bond weakly, while the third one has a dangling bond in which the acceptor level is mainly localized. The combination of the dangling bond and the weak bond provides the acceptor state in the bandgap. Since about 70% of the acceptor orbital is localized on the first neighbors of the divacancy, it makes sense to compare the spin distribution calculated for 3C with experimental values obtained for the k sites of hexagonal polytypes. This is shown in Table I with the values deduced from ENDOR in 6H SiC. (The calculated total spin density on the carbon second neighbors of the V_C part is 15.3% to be compared with the measured 7.2%. This relatively big difference is caused by the finite size of the mo-

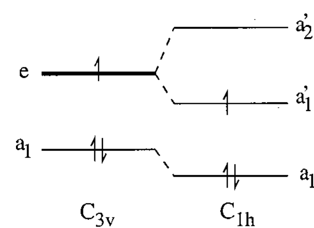

FIG. 3. The Jahn-Teller effect in the electron configuration of $B_{Si}+V_C$ in SiC.

TABLE I. Spin distribution of the acceptor level of the neutral ($B_{Si}+V_C$) complex in percentage (for notation of atoms, see Fig. 1).

Atom	Calculation	Experiment[a]
B	0.6	≈0.0
Si_1	43.7	
Si_2	12.3	
Total:	68.3	≈70–90
C_1	0.3	
C_2	0.1	
Total:	0.5	≈0.6
C_3	1.9	
C_4	2.6	
C_5	0.4	
C_6	0.6	
C_7	3.1	
Total:	15.3	≈7.2

[a]From Ref. 16.

lecular cluster, which limits the delocalization of the acceptor orbital, as witnessed by the fact that, after monotonous decrease from the center of the cluster toward the edge, the spin density slightly increases on the boundary.) The similarity between the calculated 3C and measured 6H results corroborates the analysis in Ref. 16. The strong localization explains why the difference is little between the two polytypes (and also between the cubic and hexagonal sites in 6H).

In the negatively charged state, the Si atoms around V_C decrease their positive charge relative to that in the perfect lattice. This extra negative charge is again accommodated by the weak bond between the Si_2 atoms (9.5% on each) and the dangling bond of the Si_1 atom (43.3%), pointing toward the vacancy. Therefore, 62% of the trapped charge of the ionized acceptor is localized in V_C. That means that in the $(B_{Si}+V_C)^-$ complex, the acceptor part is, in fact, the V_C, so the negative charge state can be noted as $B_{Si}+V_C^-$. The donor-acceptor recombination that gives rise to the PL spectrum occurs between centers in the same carbon sublattice resulting in a Type I spectrum. Still, B resides on the Si site as predicted by ENDOR. Thus, the contradiction of the PL and EPR results can be resolved, without invoking bistability.

In summary, we have investigated the boron-vacancy system in SiC by first principle quantum mechanical calculations. These calculations prove that a center seen in EPR/ENDOR[16] is indeed related to a deep boron acceptor, which contains B on the Si site but captures the electron on the C site. This latter fact results in a Type I spectrum observed in PL upon charge recombination between the deep boron acceptor and a nitrogen donor on the C site. The localization of the electron is strong enough to make for little difference between different sites in hexagonal polytypes and in 3C. This picture is consistent with all available experimental data.

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[1] J. M. Blank, Mater. Res. Bull. **4**, 179 (1969).
[2] G. A. Lomakina, G. F. Kholuyanov, R. G. Verenechikova, E. H. Kokhov, and Y. A. Vodakov, Fiz. Tekh. Poluprovodn. **6**, 1133 (1972).
[3] D. V. Demyanschik, G. A. Karatynina, and E. A. Konorova, Sov. Phys. Semicond. **9**, 900 (1975).
[4] M. Ikeda, H. Matsunami, and T. Tanaka, Phys. Rev. B **22**, 2842 (1980).
[5] M. M. Anikin, A. A. Lebedev, A. L. Syrkin, and A. V. Suvorov, Sov. Phys. Semicond. **19**, 69 (1985).
[6] H. Kuwabara and S. Yamada, Phys. Status Solidi A **30**, 739 (1975).
[7] W. Suttrop, G. Pensl, and P. Lanig, Appl. Phys. A: Solids Surf. **51**, 231 (1990).
[8] V. S. Ballandovich and E. N. Mokhov, Semiconductors **29**, 187 (1995).
[9] S. G. Sridhara, L. L. Clemen, R. P. Devaty, W. J. Choyke, D. J. Larkin, H. S. Kong, T. Troffer, and G. Pensl, J. Appl. Phys. **83**, 7909 (1998).
[10] T. Matsumoto, O. G. Poluektov, J. Schmidt, E. N. Mokhov, and P. G. Baranov, Phys. Rev. B **55**, 2219 (1997).
[11] J. Reinke, S. Greulich-Weber, J.-M. Spaeth, E. N. Kalabukova, S. N. Lukin, and E. N. Mokhov, Inst. Phys. Conf. Ser. **137**, 211 (1993).
[12] S. Greulich-Weber, Phys. Status Solidi A **162**, 95 (1997).
[13] T. L. Petrenko, V. V. Teslenko, A. A. Bugai, V. D. Khavryutchenko, and A. A. Klimov, Semicond. Sci. Technol. **11**, 1276 (1996).
[14] A. Fukumoto, Phys. Rev. B **53**, 4458 (1996).
[15] P. G. Baranov and E. N. Mokhov, Semicond. Sci. Technol. **11**, 489 (1996).
[16] A. Duijn-Arnold, T. Ikoma, O. G. Poluektov, P. G. Baranov, E. N. Mokhov, and J. Schmidt, Phys. Rev. B **57**, 1607 (1998).
[17] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[18] R. Jones, Philos. Trans. R. Soc. London, Ser. A **341**, 351 (1992).
[19] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[20] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
[21] R. Jones, C. Ewels, J. Goss, J. Miró, P. Deák, S. Öberg, and F. B. Rasmussen, Semicond. Sci. Technol. **9**, 2145 (1994).
[22] P. K. Sitch, R. Jones, S. Öberg, and M. I. Heggie, Phys. Rev. B **52**, 4951 (1995).
[23] C. P. Ewels, R. Jones, S. Öberg, J. Miró, and P. Deák, Phys. Rev. Lett. **77**, 865 (1996).
[24] M. Budde, B. B. Nielsen, P. Leary, J. Goss, R. Jones, P. R. Briddon, S. Öberg, and S. J. Breuer, Phys. Rev. B **57**, 4397 (1998).
[25] R. Jones, J. P. Goss, P. R. Briddon, and S. Öberg, Phys. Rev. B **56**, R1654 (1997).
[26] R. Jones and S. Öberg, Mater. Sci. Forum **143–147**, 253 (1994).

[27] S. Ögut, H. Kim, and J. R. Chelikowsky, Phys. Rev. B **56**, R11 353 (1997).
[28] A. Zywietz, J. Furthmuller, and F. Bechstedt, Phys. Status Solidi B **210**, 13 (1999).
[29] S. J. Clark and G. J. Ackland, Phys. Rev. B **56**, 47 (1997).
[30] No meaningful Mulliken analysis can be carried out on an extended GTO basis. Therefore, the one-electron eigenvectors were first projected on a contracted minimal basis using the method of R. Szokovács, J. Miró, P. Deák, and M. Pederson (unpublished).