*Materials Science Forum Vols. 353-356 (2001) pp 455-458*

*doi:10.4028/www.scientific.net/MSF.353-356.455*

# Boron Centers in 4H-SiC

B. Aradi[1], A. Gali[1], P. Deák[1], E. Rauls[2], Th. Frauenheim[2] and N.T. Son[3]

[1] Department of Atomic Physics, Technical University of Budapest, Budafoki út 8, HU-1111 Budapest, Hungary

[2] Department of Physics, Theoretical Physics, University GH Paderborn, Warburgstr. 100, DE-33095 Paderborn, Germany

[3] Department of Physics and Measurement Technology, Linköping University, SE-581 83 Linköping, Sweden

**Keywords:** Boron, Intrinsic Defects, Occupancy Level

**Abstract.** The origin of the "deep boron related acceptor level" in SiC is subject to a lot of controversy. Based on ENDOR investigations, a $B_{Si}$+$V_C$ model was suggested, while PL studies indicated the acceptor on the carbon sublattice. Our former ab initio LDA *molecular cluster* calculation showed that in the $B_{Si}$+$V_C$ complex the carbon vacancy acts as the acceptor. Now, ab initio LDA *supercell* calculations have been carried out for boron-related complexes to calculate the occupation levels in 4H-SiC. It has been found that the 0/- level for the $B_{Si}$+$V_C$ complex lies in the upper half of the gap, therefore it can be disregarded as the origin of the "deep boron-related acceptor level". Investigating other feasible boron-related complexes, $B_{Si}$+$Si_C$ appears to be the best candidate.

Boron gives rise to a shallow as well as to a deep acceptor level [1] in SiC. The "shallow boron level" was suggested to be an off-center boron substitutional on a Si site ($B_{Si}$) [2]. Low concentrations ($10^{13-14}$ $cm^{-3}$) of the center responsible for the "deep boron level" arise in boron doped epilayers grown under C-rich conditions, with higher concentrations in samples grown with high Si/C ratio [3]. From conduction-band-to-neutral-defect photoluminescence (PL) in the latter samples, the position of the one-electron level associated with the negative charge state of this center was estimated to be at $E_v + 0.655$ eV in 4H-SiC [3]. Such a transition implies acceptor character of the center.

In B-implanted p-type 6H-SiC, Deep Level Transient Spectroscopy (DLTS) has revealed a boron related deep level, called D center, [4] which, however, had donor character. B-implantation into n-type material and subsequent annealing produced concentrations in the order of $10^{16}$ $cm^{-3}$ [5]. It is usually assumed that the D center contains an intrinsic point defect besides B. It is also assumed that the "deep acceptor level" seen in PL experiments and the D center originate from the same amphoteric defect which has close lying +/0 and 0/- occupation levels. The D center was also found in the boron-doped 4H-SiC epilayers mentioned above. DLTS measurements in layers grown with low Si/C ratio put the occupancy level at $E_v + 0.550$ eV [3] (assuming $T^{-2}$ dependence of the capture cross section).

By electron spin resonance (EPR) and electron nuclear double resonance (ENDOR) experiments [6, 7] a boron related complex with a B atom on a Si site next to a C vacancy ($B_{Si}$+$V_C$) has been recently identified in 6H material. This complex was suggested [6, 7] as the origin of the "deep boron level".

3C-SiC samples co-doped with N and B have shown a Type I PL spectrum for the deep B acceptors recombining with the shallow nitrogen donors [8], indicating that the ionized donor and acceptor occupy the same sublattice. Since nitrogen sits on a carbon site, the deep B center was associated with a complex containing B at a C site.

Regarding the controversy in the experimental information about the "deep boron level", our paper aims at investigating boron related complexes by means of *ab initio* electronic structure calculations in 4H-SiC. We were looking for a complex

1. with amphoteric electronic activity

2. having a +/0 (donor) occupation level around $E_v + 0.55$ eV
3. having a one-electron level at $E_v + 0.66$ eV in the negative charge state
4. with acceptor activity connected to the carbon site
5. occurring more frequently in silicon-rich material or after implantation

Taking this experimental information into account we studied stable complexes of boron with vacancies and antisites.

Ab initio calculations in the local density approximation of density functional theory [9] (DFT) were performed using the FHI98MD code [10], which applies plane waves to expand the one-electron wave functions. A kinetic energy cut-off of 36 Ry was used in conjunction with Troullier-Martins norm conserving soft-core pseudopotentials [11]. Tests on carbon pseudopotentials have shown the cut-off of 36 Ry to provide convergent results [12]. 4H-SiC was modeled by a 96-atom supercell (SC). Summation over the reduced Brillouin-zone of the supercell was carried out using a 2x2x2 MP scheme [13]. DFT is known to uniformly underestimate the position of the conduction band (CB) states with respect to the valence band maximum (VBM). The band gap in our case was 2.3 eV compared to the experimental 3.3 eV. Defect states are a mixture of states from the CB and VB, therefore defect levels in the band gap have been shifted by $(3.3\text{ eV} - 2.3\text{ eV}) \cdot S$, where $S$ is the overlap of the defect state with the CB states [14]. The total energy was then corrected with this shift, times the occupation number of the defect state. Another correction was made necessary because of the dispersion caused by the interaction of repeated defects in the SC model. An approximate position of the "isolated" defect level was found by a tight binding fit to the energies calculated at different k-points [15]. The total energy was then corrected by the differences between this value and the defect levels calculated at the individual k-points, times the occupation numbers. The dispersion in our calculations were always less than 0.2 eV. For spin half systems the error due to the lack of spin-polarization in the total energy (and in one-electron levels) is estimated to be $-0.1$ eV, and this value was added as correction. The occupation levels were determined from the difference of the total energies in different charge states.

In an earlier paper we have shown [16] by *ab initio* molecular cluster calculations that the $B_{Si}$+$V_C$ complex is more stable both in the neutral and in the negatively charged state than the $V_{Si}$+$B_C$ system (see Fig. 1.a,b). It was also shown that the spin distribution of the $B_{Si}$+$V_C$ complex corresponds indeed to the EPR/ENDOR signals found in Ref. [7]. In addition, it was pointed out that the acceptor activity is connected to the carbon vacancy. Now, we have calculated the $B_{Si}$+$V_C$ complex in our supercell to obtain its one-electron and occupation levels with respect to the gap. The calculations were carried out at the cubic site with the complex oriented along the c-axis. After relaxation, the symmetry of this complex is $C_{1h}$ due to a Jahn-Teller distortion from $C_{3v}$. In the neutral charge state a singly occupied one-electron level was found in the gap at $E_v + 2.3$ eV, associated with the Si neighbors of $V_C$. The corresponding +/0 and 0/- occupation levels are at $E_v + 1.9$ eV and $E_v + 2.1$ eV, respectively. These values are much too high, so the $B_{Si}$+$V_C$ complex can be disregarded after all as the origin of the deep boron level! Still, it is a stable amphoteric defect which was detected in EPR and ENDOR. However, this complex is more likely to act as a deep donor.

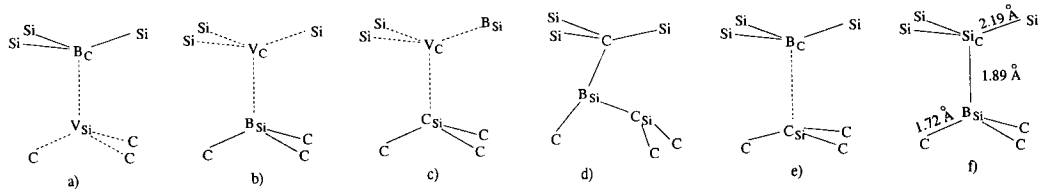


**Fig. 1.** The investigated complexes: a) $V_{Si}$+$B_C$, b) $B_{Si}$+$V_C$, c) $C_{Si}$+$V_C$+$B_{Si}$, d) $C_{Si}$-$B_{Si}$ pair, e) $C_{Si}$+$B_C$, f) $B_{Si}$+$Si_C$

After excluding boron next to a carbon vacancy, B next to $V_{Si}$ could have been investigated.

However, not only showed the molecular cluster calculation [16] $V_{Si}$+$B_C$ instable with respect to $B_{Si}$+$V_C$ by a large margin, $V_{Si}$ itself is metastable with respect to $V_C$+$C_{Si}$ [17, 18]. Therefore, next we have investigated the latter complex with a Si atom in the neighborhood of $V_C$ substituted by B, forming the $C_{Si}$+$V_C$+$B_{Si}$ complex (see Fig. 1.c). This defect turns out to be stable with a singly occupied level in the band gap at $E_v + 1.5$ eV in the neutral charge state. The level can be associated with the dangling bond on $C_{Si}$. This is a bit surprising, since carbon dangling bonds usually have levels close to the VBM. However, due to the back relaxation of $C_{Si}$ towards the plane of its carbon neighbors, its dangling bond is almost entirely $p$-like, unlike the usual $sp^3$ hybrids. The 0/- occupation level is at $E_v + 2.0$ eV. Therefore, this defect can also be discarded as the origin of the "deep boron level".

The lowest energy intrinsic point defects after the vacancies are antisites. First we have investigated boron next to a carbon antisite, both as an interstitial and as a substitutional. The most stable interstitial configuration was the $C_{Si}$-$B_{Si}$ split-interstitial pair (see Fig. 1.d). It is a stable defect with low formation energy, but it is more a donor than an acceptor. It has a singly occupied level at $E_v + 2.4$ eV in the neutral charge state, associated with a $p$-like dangling bond on $C_{Si}$. The position of the level disqualifies this complex as well. Placing boron at a substitutional site next to $C_{Si}$ gives the $C_{Si}$+$B_C$ structure (see Fig. 1.e). This defect is metastable with respect to $B_{Si}$ (which can be obtained by interchanging the C anti-site and the B atom) by $\sim$ 4 eV. Besides, the acceptor activity of $C_{Si}$+$B_C$ is connected to $C_{Si}$, i.e., to the silicon sublattice, so it can also be disregarded as a candidate for the "deep boron level".

Finally, we have investigated substitutional boron next to a silicon antisite at the cubic site, oriented along the c-axis (see Fig. 1.f). The $B_{Si}$+$Si_C$ complex has $C_{3v}$ symmetry. Similarly to the case of the isolated $Si_C$ [19], we find localized one-electron levels in the gap, relatively close to the VBM. The highest one at $E_v + 0.60$ eV is singly occupied in the neutral charge state. Fig. 1.f) shows the relaxed structure in the neutral charge state. In the negatively charged state the Si-B distance becomes somewhat longer than in the neutral state, but the geometry is essentially the same. The orbital with the unpaired electron in the neutral and accommodating the extra charge in the negative charge state is strongly localized on $Si_C$. Therefore, the acceptor activity is connected with the carbon sublattice. The 0/- occupation level is at $E_v + 0.64$ eV and the position of the ionized acceptor level is at $E_v + 0.73$. The defect can also be positively ionized. The +/0 occupation level is at $E_v + 0.53$ eV.

Considering the accuracy of our calculations, these energy values, i.e., the +/0 occupation level at $E_v + 0.53$ eV and the one-electron level in the negative charge state at $E_v + 0.73$ eV compare rather nicely with the experimental values of $E_v + 0.55$ eV and $E_v + 0.66$ eV, respectively. Therefore, the $B_{Si}$+$Si_C$ complex meets the criteria 1–4 mentioned earlier. As for criterion 5, the $B_{Si}$+$Si_C$ complex implies silicon rich material. It has to be noted, however, that interchanging the boron atom with $Si_C$ in this complex, $B_C$ is obtained, which is significantly lower in energy. As a consequence, the formation of $B_{Si}$+$Si_C$ complexes in equilibrium is unlikely. However, if created in some non-equilibrium process during growth, it will remain stable. Recent work on antisite pairs [20] has shown that interchanging Si and C atoms in SiC requires an energy barrier of $\sim$ 10 eV. The interchange of $B_{Si}$ and $Si_C$ is expected to have an activation energy in this range as well. The $B_{Si}$+$Si_C$ complex may well arise in the activation process of implanted boron interstitials. Boron is known to prefer the silicon site [21] but emission of an interstitial Si atom is energetically very costly. Calculations on tetrahedral interstitials in the neutral charge state [22] predict $C_i$ to be $\sim$ 6 eV lower in energy than $Si_i$. More recent results [23] give smaller differences but for n-type SiC (high Si/C ratio) also predict $C_i$ lower in energy than $Si_i$. Therefore, the following reaction seems plausible: $B_i \rightarrow B_{Si} + Si_i \rightarrow (B_{Si}+Si_C) + C_i$.

To summarize, several boron-related complexes have been investigated to find the microscopic origin of the deep boron level. We have found that the $B_{Si}$+$V_C$ complex seen in ENDOR is an amphoteric defect but it is rather a donor than an acceptor. So there ought to be a boron related donor-like level at around $E_v + 1.9$ eV in 4H-SiC! We have found only one boron-related complex with donor

and acceptor occupation levels around $E_v + 0.6$ eV. In agreement with PL results on the "deep boron level", in this $B_{Si}$+$Si_C$ the final state of the conduction-band-to-neutral-defect photoluminescence is calculated to be at $E_v + 0.73$ eV and is strongly localized on the carbon site. The complex is amphoteric, with a donor-like +/0 occupation level at $E_v + 0.53$ eV, in good agreement with values obtained for the D center in 4H-SiC. The composition of this defect implies higher concentrations in silicon-rich material, and it is likely to be created during B-implantation. It has to be noted, though, that formation of $B_C$ substitutionals is energetically more favorable than the creation of $B_{Si}$+$Si_C$ complexes. Still, among the investigated complexes, $B_{Si}$+$Si_C$ fits the experimental information available on the "deep boron level" best.

**Acknowledgement** The authors are indebted to Prof. J. W. Choyke for many valuable discussions. Support by the Hungarian OTKA T-22139 and FKFP 0289/97 grants as well as the bilateral German-Hungarian (DFG -MTA No. 118) and Swedish-Hungarian (IVA-MTA No. 36) projects are appreciated. This work was also supported by a grant from the National Supercomputing Center (Sweden).

## References

[1] J. M. Blank, Mat. Res. Bul. 4 (1969), p. 179.

[2] S. Greulich-Weber, phys. stat. sol. (a) 162 (1997), p. 95.

[3] S. G. Sridhara *et al.*, J. Appl. Phys. 83 (1998), p. 7909.

[4] W. Suttrop, G. Pensl, and P. Lanig, Appl. Phys. A: Solids Surf. 51 (1990), p. 231.

[5] M. Gong *et al.*, Appl. Phys. Lett. 72 (1998), p. 2739.

[6] P. G. Baranov and E. N. Mokhov, Semicond. Sci. Technol. 11 (1996), p. 489.

[7] A. Duijn-Arnold *et al.*, Phys. Rev. B 57 (1998), p. 1607.

[8] H. Kuwabara and S. Yamada, Phys. Status Solidi A 30 (1975), p. 739.

[9] W. Kohn and L. J. Sham, Phys. Rev. 140 (1965), p. A1133.

[10] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comp. Phys. Comm. **107** (1997), p. 187.

[11] N. Troullier and J. L. Martins, Phys. Rev. B 43 (1991), p. 1993.

[12] M. Bockstedte, private communication.

[13] H. J. Monkhorst and J. K. Pack, Phys. Rev. B 13 (1976), p. 5188.

[14] G. A. Baraff and M. Schlüter, Phys. Rev. B 30 (1984), p. 1853.

[15] S. G. Louie, M. Schlüter, J. R. Chelikowski, and M. L. Cohen, Phys. Rev. B 13 (1976), p. 1654.

[16] A. Gali, P. Deák, R. P. Devaty, and W. J. Choyke, Phys. Rev. B 60 (1999), p. 10620.

[17] E. Rauls *et al.*, phys. stat. sol. (b) 217/2 (2000), p. R1.

[18] M. Bockstedte and O. Pankratov, Mater. Sci. Forum 338-342 (2000), p. 949.

[19] L. Torpo, S. Pöykkö, and R. M. Nieminen, Phys. Rev. B 57 (1998), p. 6243.

[20] E. Rauls *et al.*, Mater. Sci. Forum, this volume (2000).

[21] D. J. Larkin and V. A. Laki, J. Electron. Mater. 24 (1995), p. 289.

[22] C. Wang, J. Bernholc, and R. F. Davies, Phys. Rev. B 38 (1988), p. 12752.

[23] A. Mattausch and V. A. Laki, this volume (2000).

**Silicon Carbide and Related Materials 2000**
10.4028/www.scientific.net/MSF.353-356

**Boron Centers in 4H-SiC**
10.4028/www.scientific.net/MSF.353-356.455