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2001 J. Phys.: Condens. Matter 13 9019

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Boron and aluminium doping in SiC and its passivation by hydrogen

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Received 2 May 2001

Published 20 September 2001

Online at stacks.iop.org/JPhysCM/13/9019

Abstract

Extensive calculations regarding the formation energy of interstitial hydrogen and hydrogen–vacancy complexes in different charge states have been carried out using the local density approximation to *ab initio* density functional theory with a plane-wave basis and norm-conserving pseudopotentials on supercells of cubic (3C) SiC. Based on these results the hydrogen concentration of as-grown or H-plasma treated SiC is estimated and its effect on the net carrier concentration is given. Incorporation of B and Al in or without the presence of hydrogen has been investigated in hexagonal (4H) SiC supercells. The possible origins of the shallow and deep boron acceptors is discussed. It is found that the presence of boron promotes hydrogen incorporation during growth in the form of passive B + H complexes. The same is not true for Al. If Al + H complexes are formed (say, after H-plasma treatment), the structure of this complex is different from that of the B + H complexes. The calculated difference between the dissociation energies is 0.9 eV.

1. Introduction

Due to its maturing technology, silicon carbide is at present the best candidate for becoming the semiconductor material of high-power, low-loss electronic devices. Since diffusion is too slow in SiC under 1300 °C, doping is carried out either by implantation or in growth. Both procedures involve problems with activation. The substitutional incorporation of the dopant atom in one or the other sublattice is promoted by tuning the Si/C ratio in growth or by co-implantation of Si or C. By ensuring a supply of silicon or carbon vacancies, it is made easier for the dopant to compete for the site where it is destined to go (site competition mechanism [1]). Among the p-type dopants, the behaviour of Al is relatively predictable: it prefers the silicon site (Al_{Si}), where it fits in more conveniently, and produces a shallow acceptor level between $E_V + 0.19$ – 0.25 eV in the different polytypes [2]. Boron, on the other hand, has been reported to occupy

both the silicon and the carbon site, alas, with a preference for the Si site. If SiC is grown under Si-rich conditions in CVD (offer of C sites for B), the boron incorporation is substantially lower than in the case of C-rich conditions (offer of Si sites) [3]. Boron produces both a shallow and a deep acceptor centre, along with two paramagnetic centres¹. The (0/−) occupation level of the shallow boron acceptor was found at $\sim E_V + 0.30$ eV in 4H-SiC with deep level transient spectroscopy (DLTS) [4]. DLTS also indicates a boron related deep acceptor with the (0/−) occupation level at $\sim E_V + 0.55$ eV (in 4H-SiC) while the one electron level of the negatively charged state of this centre was obtained at $E_V + 0.65$ eV from donor–acceptor recombination luminescence [5]. This deep acceptor centre is mostly obtained after boron implantation but has also been seen in samples grown under Si-rich conditions [6]. Paramagnetic resonance studies have also revealed two boron related centres. Both show negligible spin localization on the boron atom. The first centre [7] seems to contain a carbon dangling bond and is assumed to originate from a silicon site boron substitutional (B_{Si}) in a strongly off-centre position (C_{3v} symmetry). This B_{Si} defect is usually identified with the shallow boron acceptor, although no direct correlation has been established between the electron paramagnetic resonance (EPR) and the DLTS centres. The off-centre behaviour is used to explain the deeper level of B_{Si} with respect to Al_{Si} . The other boron-related paramagnetic centre [8] seems to contain a silicon dangling bond and was assigned to B_{Si} next to a carbon vacancy ($B_{Si} + V_C$). It was speculated that ($B_{Si} + V_C$) might be the origin of the deep boron-related acceptor activity, even though no correlation to electrical measurements have been proven.

Hydrogen is an ‘intrinsic’ impurity of the SiC growth processes. In nominally hydrogen free growth methods (bulk growth) the graphite parts of the reactor can be the source of H contamination. At the temperatures used there (~ 2400 °C), this hydrogen can be released in atomic form. CVD processes use hydrogen containing precursors for Si, C, and the p-type dopants as well—mostly diluted in a H_2 carrier gas. At the typical temperatures of CVD growth (1400–1700 °C) only a small fraction of H_2 molecules dissociate, but due to the reactions between the precursors in the vicinity of the SiC surface, about 1% of the hydrogen may occur in atomic form. The incorporation of hydrogen into the crystal might affect doping efficiency by influencing the site competition process, by passivating or compensating the dopants, or by passivating vacancy related traps. Direct evidence for the presence of hydrogen in as-grown CVD samples were found only in B-doped p-type SiC with SIMS. Hydrogen seems to be incorporated together with boron, passivating or compensating about half of the boron content [3]. However, even in B-doped samples grown in a nominally hydrogen free environment, hydrogen related photoluminescence (H-centre: usually assigned to hydrogen in a silicon vacancy, $V_{Si} + H$) appears, after the ion bombardment of a SIMS investigation [9]. The hydrogen content is again proportional with the [B] concentration. This indicates that hydrogen is incorporated together with boron in the first place. Hydrogen introduced by implantation [10] or low-temperature plasma anneal [11] resulted in a complete passivation of p-type doping by the formation of $Al + H$ or $B + H$ complexes. The experimentally observed reactivation energy of these complexes seems to differ, however, by about 1 eV. In contrast, hydrogenation attempts were mostly unsuccessful in n-type SiC [12]. High density direct current plasma treatment [13] or high dose implantation [14] causes a decrease in the free carrier concentration due to the appearance of electron traps in n-type samples.

The purpose of this paper is to use first principles model calculations to shed light on the anomalous behaviour of boron, on the one hand, and the effect of hydrogen on the

¹ The word ‘centre’ is used here in the sense of the origin of an experimentally observed signal. The actual defect or defect complex giving rise to these signals will be given by a formula, e.g. $B_{Si} + H_{BC}$, describing the composition and the geometrical configuration. Such a defect or complex will be referred to as a ‘model’ of a given centre as long as the identification is not confirmed.

doping efficiency, on the other. The calculations are based on density functional theory in the local density approximation (LDA), in conjunction with the use of norm-conserving pseudopotentials. The FHI98MD code [15], which utilizes a plane wave expansion of the one-electron states, was used to carry out calculations for periodic supercells containing the defects. For 3C–SiC 128 atom supercells (SC), for 4H–SiC 96 atom SC-s were used, with kinetic energy cut-offs between 30 and 36 Ry and Brillouin zone summations for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ Monkhorst–Pack sets. Details of the calculation including the applied corrections (for LDA gap, SC dispersion, spin polarization, etc) are given in [16]. The paper is organized as follows. In section 2 a short summary is given of the various forms of hydrogen in SiC, their electrical activity and expected concentration. Section 3 summarizes results on the spin distribution and electrical activity of boron related complexes. Finally, in section 4 complex formation between B, Al and H is considered.

2. Hydrogen in SiC

We have carried out an extensive study of hydrogen defects in 3C–SiC [16]. One or two hydrogen interstitials as well as hydrogen atoms in silicon and carbon vacancies have been considered in all possible charge states. Interstitial atomic hydrogen has also been investigated in 4H–SiC [17].

Excluding interaction with the dopants, interstitial hydrogen appears to have the lowest formation energy. Unlike in other semiconductors, up to a Fermi-level position of about $E_V + 1.3$ eV, the positively charged isolated interstitial hydrogen atom (in an antibonding position behind a carbon atom) is the most stable; above that the interstitial H₂ molecule (at the T site surrounded by Si atoms). Atomic interstitial hydrogen changes charge state at about $E_V + 2.3$ eV. In 4H–SiC it becomes negatively charged (negative U), while there is a small stability window for neutral H in 3C–SiC. (H[−] is near the T site surrounded by Si atoms.) Accordingly, H_i is a relatively shallow (effective mass like) donor in cubic ($E_g^{3C} = 2.4$ eV) but a deep amphoteric trap in hexagonal ($E_g^{4H} = 3.3$ eV) material. As a consequence, hydrogen can, in principle, compensate both cubic and hexagonal p-type, but only hexagonal n-type material. Complex formation with charged dopants are facilitated in a similar manner.

Among the vacancy–hydrogen complexes, V_C + nH ones are preferred in p-type and V_{Si} + nH ones in n-type SiC. The formation energy decreases for the latter and increases for the former with increasing *n*. V_{Si} + nH complexes are electron traps for *n* = 1, 2 but V_{Si} may, in principle, accommodate four H atoms which can passivate it completely. On the contrary, only two hydrogen atoms can bind to V_C, in a three-centre bond with a pair of Si-neighbours each [18]. These complexes are hole traps. The formation energy of V + H complexes are high relative to interstitial hydrogen. Although, as far as the formation energies are concerned, V_C + H is more favourable than V_{Si} + H, if both vacancies are already present, hydrogen is preferentially captured by V_{Si}. Both vacancies are capable of spontaneously dissociate H₂.

Based on the calculated formation energies (as a function of Fermi-level and chemical potentials), a rough estimate can be given for the hydrogen concentrations under various circumstances. Our estimation neglects temperature effects within the crystal and assumes equilibrium with a gas containing a given partial pressure of (atomic or molecular) hydrogen at a given temperature. Figure 1(a) gives concentrations in 3C–SiC for $p[\text{H}_a] = 0.01$ atm and $T = 1400$ °C simulating the circumstances of CVD growth. Figure 1(b) gives data more or less relevant to low-temperature H-plasma treatment, i.e. $p[\text{H}_a] = 0.03$ atm and $T = 300$ °C. As can be seen, hydrogen incorporation during growth can be expected to be significant only in p-type samples, in the form of interstitial H⁺. These are compensating centres

but their concentration is two orders of magnitude lower than the free carrier concentration. In contrast, hydrogen plasma treatment can result in complete compensation of p-type SiC. In n-type material, however, only $V_{Si} + nH$ complexes—which act as electron traps—are introduced. They can effectively diminish the free carrier concentration. These results are in good qualitative agreement with the experimental findings mentioned in the introduction, except for the hydrogen concentration in B-doped p-type material. The interaction of B and H has been so far excluded, but they may be incorporated together as a B + H complex, increasing the total amount of hydrogen in the sample. To investigate this question, first the equilibrium configurations of boron have to be determined.

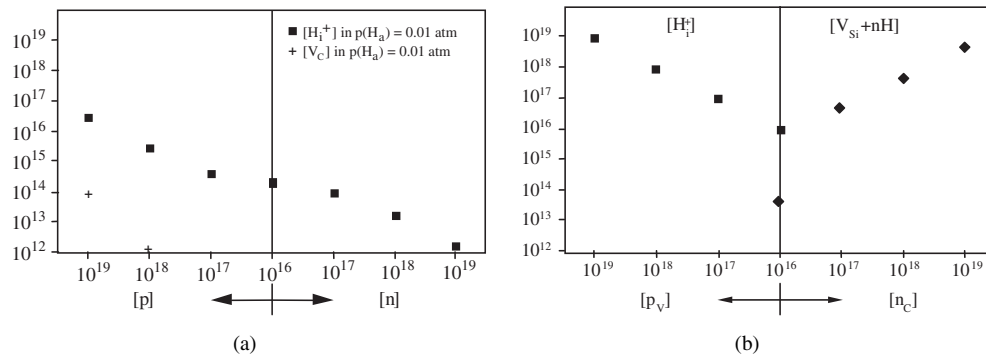


Figure 1. The estimated concentration (cm^{-3}) of H-related defects as a function of net carrier concentration (cm^{-3}) in 3C-SiC, being in equilibrium with (a) $p = 0.01$ atm atomic hydrogen gas at 1400°C and (b) $p = 0.03$ atm atomic hydrogen gas at 300°C . Complex formation between hydrogen and the dopant was disregarded. The position of the Fermi-level was determined self-consistently. Species not shown have concentrations lower than 10^{12} cm^{-3} .

3. Boron centres in 4H-SiC

As mentioned in the introduction, a shallow and a deep acceptor centre, as well as two paramagnetic centres related to boron have been found experimentally. One of the paramagnetic centres was assigned to the B_{Si} defect and this is usually assumed to be the origin of the shallow acceptor centre as well. The assignment of the other paramagnetic centre to $B_{Si} + V_C$ was also confirmed by calculations [19]. The two acceptor centres have their respective ($0/-$) occupation levels at about $E_V + 0.30$ and $E_V + 0.55$ eV. From donor–acceptor recombination luminescence it is known that the deep acceptor activity should be connected with the carbon sublattice. It is also known that the shallow acceptors are more likely to occur in samples grown under C-rich conditions, while Si-rich conditions or implantation produce more of the deep acceptors. With these facts in mind we have studied a large variety of boron + intrinsic point defect complexes: B_{Si} , B_C , $B_{Si} + V_C$, $V_{Si} + B_C$, $B_{Si} + V_C + C_{Si}$, $(B_{Si} + C_{Si})_{split}$, $B_{Si} + Si_C$, and $C_{Si} + B_C$ [20]. Only four of these B_{Si} , B_C , $B_{Si} + V_C$, and $B_{Si} + Si_C$ (see figure 2) appear to have relevance to the boron related centres observed experimentally so far.

The $B_{Si} + V_C$ complex turns out to have a ($0/-$) occupation level at about $E_V + 2.1$ eV. Even regarding the possible errors in calculating occupation levels, this disqualifies it as the model of the deep boron acceptor centre. However, since this complex can definitely be identified with one of the observed paramagnetic centres, such an electron trap has still to be found by electrical or optical measurements! For the $B_{Si} + Si_C$ complex the calculation resulted in a

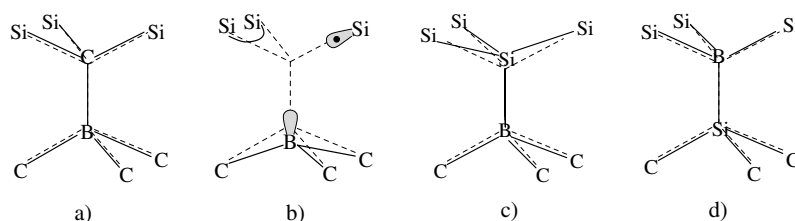


Figure 2. The geometry and bonding in the (a) B_{Si} , (b) $B_{Si} + V_C$, (c) $B_{Si} + Si_C$, (d) B_C defects. Dashed lines show the original lattice bonds.

(0/−) occupation level at $E_V + 0.64$ eV. The acceptor activity is related to a state strongly localized to Si_C , i.e., to the carbon sublattice. The corresponding one-electron level in the negative charge state is at $E_V + 0.73$ eV. These values fit the DLTS (0.55 eV) and PL (0.65 eV) results for the deep boron acceptor reasonably well. However, $B_{Si} + Si_C$ is an isomer of B_C and it is about 3 eV less stable than that. Therefore, even though $B_{Si} + Si_C$ might occur after boron implantation, it is hardly likely to form during growth.

Of course, the obvious candidates as models of the shallow and deep boron acceptor centres would be the simple substitutionals B_{Si} and B_C . Our calculations give, indeed, a 0.3 eV difference between their (0/−) occupation levels, however, both of them seem to be only stable in an on-centre configuration with considerable spin density on the boron atom. Bockstedte *et al* have shown in spin-polarized 216 atom SC calculations for 3C–SiC that—applying the technique of Makov and Payne [21] to correct the errors of the mandatory charge compensation under periodic boundary conditions in case of charged defects—the (0/−) occupation levels of B_{Si} and B_C can be obtained at $E_V + 0.2$ and 0.43 eV, respectively [22]. These values seem to be close to the ones found in 4H–SiC. Using a constrained relaxation technique they were also able to find a shallow minimum of the total energy, with the boron atom being slightly off-centre. However, the spin density is still far from being negligible on boron. These results shed some doubt on the identification of B_{Si} with the shallow acceptor *and* the paramagnetic centre observed by Adrian *et al* [7] but the discrepancy may well originate from the deficiencies of today's theoretical tools and capabilities. If we accept B_{Si} as the origin of the shallow boron acceptor, B_C appears to be a good candidate for the deep one.

4. Interaction of H with B and Al

In considering the concentration of hydrogen incorporated into SiC during CVD growth, we have first excluded the interaction of H with the dopants. According to experiments, however, B-doped samples contain hydrogen in the same order of magnitude as boron, and they form electrically passive complexes. It was assumed that B + H complexes are incorporated into the SiC crystal in the first place. In the case of Al, hydrogen passivation was proven only after post-hydrogenation.

We have investigated complexes of H with the p-type dopants B_{Si} , Al_{Si} (assuming B_{Si} to be the origin of the shallow boron acceptor) in 4H–SiC. As can be seen in figure 3, the most stable configurations are different in the two cases but both are electrically inactive, i.e., both acceptors can be passivated by hydrogen. Hydrogen is bonded to one of the next-neighbour carbon atoms but 'on different sides', i.e., H is in a bond-centre position in the former and in an antibonding one in the latter. Obviously, the larger Al atom does not leave space for H to be on the bond centre site as next to the smaller B atom. As a consequence, these complexes

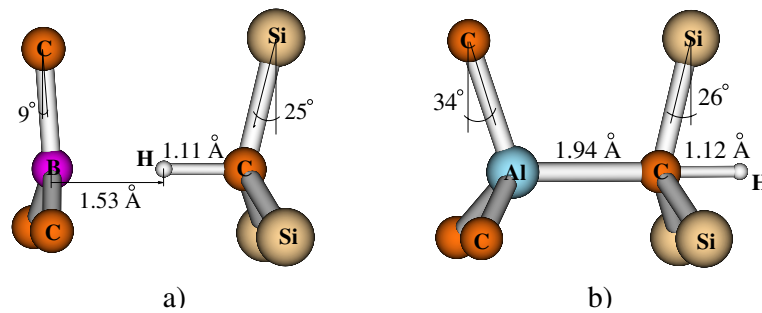


Figure 3. The geometry of the most stable acceptor–hydrogen complexes at the hexagonal site of 4H-SiC: (a) $B_{Si} + H_{BC}$, (b) $Al_{Si} + H_{AB(C)}$.

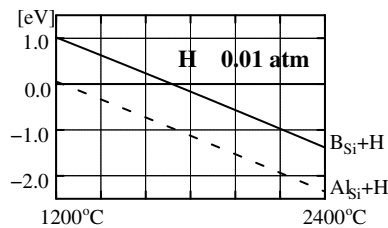


Figure 4. The difference in the energy of formation between the isolated acceptor and the acceptor–hydrogen complex, $E_{form}(X) - E_{form}(X+H)$, as a function of temperature, assuming equilibrium of 0.01 atm atomic hydrogen with a 4H-SiC crystal.

have very different energetics. First of all, the dissociation energies are different. One has to consider that in p-type SiC isolated hydrogen is positive and the acceptors are negatively charged. Therefore, the dissociation reaction is

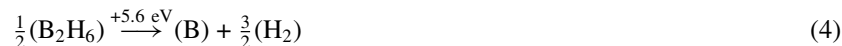
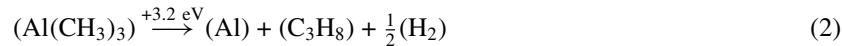


Due to the long range Coulomb interaction between charged defects, ‘isolated’ constituents cannot be calculated in the same supercell. Using the total energies of separate supercell calculations (one for X^- , H^+ , and $X + H$, each as well as a perfect one), the calculated energy difference between the isolated charged defects and the neutral complex suffers strongly from the error committed by the charge compensation in the case of the charged defects. Since the error has the same sign for both charge states, they add up. Still, the calculated difference of the dissociation energies for $B_{Si} + H_{BC}$ and $Al_{Si} + H_{AB(C)}$, 0.9 eV, are very close to the experimentally observed difference in reactivation energies, ~ 1 eV [10].

The binding energies of the acceptor–hydrogen complexes (1.6 and 0.7 eV for $B_{Si} + H_{BC}$ and $Al_{Si} + H_{AB(C)}$, respectively—to be compared to the experimental reactivation energies, 2.65 and 1.66 eV) indicate that energy may be gained by incorporating them together during growth. Since it is difficult to estimate the chemical potential of B or Al in CVD growth, we have calculated the difference of the formation energies of the acceptor–hydrogen complexes ($X+H$) and the isolated acceptors (X). The result is shown in figure 4 as a function of temperature assuming 1% atomic H in the CVD growth chamber. As can be seen, for aluminium the difference is always negative, i.e., the incorporation of isolated Al_{Si} is always more favourable than that of $Al_{Si} + H_{AB(C)}$. In contrast to that, in the temperature range of CVD growth, the difference for boron is positive, so the incorporation of $B_{Si} + H_{BC}$ is more favourable than that of B_{Si} . That means that, unlike aluminium, boron promotes hydrogen into the

crystal and they will have comparable concentrations, in agreement with the experimental observation.

In obtaining the above result, we used two approximations: the assumption of equilibrium during growth and the neglect of temperature effects in the crystal. Especially the second one is serious: the acceptor–hydrogen complexes with 2.65 and 1.66 eV activation energy for dissociation are not expected to stay together at the temperature of CVD growth. Taking kinetic factors into account, however, one has to consider the real chemical composition of the gas phase. The source of the p-type dopant is typically diborane (B_2H_6) or TMA ($Al(CH_3)_3$). These molecules may also dissociate at high temperature. Using standard heat of formation data in Born–Haber type cycles gives:



It can be seen that dissociation leading to BH and AlH is more likely than the production of the free atoms B and Al, i.e., the supply of BH molecules is much larger than that of B atoms during CVD. (Note, that the ratio $[AlH]/[Al]$ is 1–2 orders of magnitude lower than that of $[BH]/[B]$ at CVD temperatures.) Therefore, we may conclude that B and H may indeed be incorporated together.

5. Summary

Using *ab initio* LDA supercell calculations we have given estimates of the equilibrium concentration of hydrogen in SiC after CVD growth and after H-plasma treatment. We have explained the different effects of hydrogen onto the free carrier concentration in boron and aluminium doped p-type and in n-type samples. To confirm the assignment of the shallow boron acceptor centre to B_{Si} and to find the origin of the deep boron acceptor needs further investigations.

Acknowledgments

Fruitful discussions with A W R Leitch, W J Choyke, Nguyen Tien Son and M Bockstedte are appreciated. This work has been supported by the Hungarian grants OTKA- T032174 and FKFP 0289/97, the bilateral program between Hungary and South Africa (DAK 7/98), as well as grants from the Pittsburgh Supercomputer Center (PHY970006P) and the Swedish National Supercomputer Center (2000018).

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