Formation energies, abundances, and the electronic structure of native defects in cubic SiC

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The relative abundance of native point defects in cubic SiC has been studied via *ab initio* calculations as a function of composition and the Fermi-level position. For Si-rich cubic SiC, the Si_C antisite is the dominant defect in n-type material, while the carbon vacancy, which is a double donor, dominates in p-type material. These results explain the experimentally observed low doping efficiencies of acceptors and the strong self-compensation effects in Si-rich cubic SiC. In C-rich SiC, the dominant defect is the electrically inactive C_{Si} antisite, regardless of the position of the Fermi level. The slightly C-rich cubic SiC is thus a more suitable material for p-type doping.

Silicon carbide has long been known for its potential as a wide-band-gap semiconductor material for high-temperature, high-power, and high-frequency applications. It exists in a variety of close-packed, one-dimensional stacking arrangements or polytypes, the most common ones being the cubic (zinc-blende) β-SiC and the hexagonal $6H$-SiC structure.[1] Analysis of lattice parameters and densities of several SiC polytypes indicate that β-SiC is non-stoichiometric and Si rich.[1] The deviation from stoichiometry has been estimated to be less than 1%. If these analyses are accurate, the concentrations of native defects in β-SiC are relatively high. One of the purposes of this paper is to determine, via *ab initio* calculations of defect energetics, the dominant native point defects in β-SiC and their effect on the electronic properties. The understanding of these effects is particularly important in β-SiC, due to the expected deviations from stoichiometry and the need to improve doping efficiencies of acceptors.[2,3]

At low concentrations, the defect concentration is proportional to the Boltzmann factor $\exp(-E_f/kT)$, where E_f is the formation energy of the defect. Under non-stoichiometric conditions, however, the most abundant native defects will be those with the lowest formation energy per accommodated atom of the excess component. The concentration of even low-formation-energy defects, which act in the opposite direction will be suppressed.

The problem can be constructed as a set of reaction equilibria,[4] but the accuracy of current electronic structure techniques allows only for the determination of the dominant defects, rather than the prediction of the absolute defect concentrations. However, the knowledge of defect energetics is still sufficient to explain and/or predict a number of the electronic properties of cubic SiC as a function of its composition.

The present results were obtained using the self-consistent pseudopotential method to calculate the total energy of a supercell containing the various native defects. The formation energy of a specific defect was extracted from the difference in total energies between the supercell containing the defect and the one corresponding to a perfect crystal.[5] The self-consistent pseudopotential method has previously been used for the prediction of ground-state properties of pure β-SiC (Refs. 6-8). However, due to the lack of core p electrons in the carbon atoms, a relatively large number of plane waves was required. In our supercell calculations we have used a softer pseudopotential[9] of the Hamann-Schluter-Chiang type,[10] which reproduces well the results of the previous calculations[6-8] (see Table I), while allowing for supercell calculations with the cell sizes of up to 32 atoms. The plane-wave cutoffs were 14 and 28 Ry, respectively, for the waves included directly and by perturbation theory. The same potential and

TABLE I. A comparison of the calculated structural parameters of cubic SiC with other calculations and experiment.

	Present $E_1 = 14$ Ry $E_2 = 28$ Ry	Ref. 6 $E_1 = 30$ Ry	Ref. 7 $E_1 = 24$ Ry $E_2 = 48$ Ry	Ref. 8 $E_1 = 60$ Ry	Expt.[a]
E_{coh} (eV)	6.7			6.7	6.34
a_0 (Å)	4.36	4.36	4.33	4.36	4.36
B_0 (Mbar)	2.35	2.00	2.49	2.12	2.24
B_0'	2.5	7.3	3.2	3.7	

[a]As quoted in Ref. 8.

cutoffs have also been used for the calculation of structural properties of diamond and its self-diffusion activation energies.[11] Due to the larger size of the Si atom, the calculations for SiC are more extensive, with the number of plane waves included directly and by perturbation theory being 1880 and 5540, respectively, for a supercell corresponding to 32 atoms in the perfect crystal. The results for vacancies and antisites were obtained using a 32-atom supercell, while a 16-atom supercell was used for the interstitials, since their formation energies are substantially larger. Symmetry was used to reduce the amount of the computational effort to a manageable level.

We have considered eight point defects which preserve the tetrahedral symmetry of the perfect crystal (see Fig. 1). They are carbon vacancy (V_C), silicon vacancy (V_{Si}), Si_C antisite, C_{Si} antisite, a tetrahedral interstitial silicon atom surrounded by four Si atoms (Si_{TSi}), a tetrahedral interstitial silicon atom surrounded by four C atoms (Si_{TC}), a tetrahedral interstitial carbon atom surrounded by four Si atoms (C_{TSi}), and a tetrahedral interstitial carbon atom surrounded by four C atoms (C_{TC}). The calculated formation energies for these defects in their neutral charge states are listed in Table II. These energies are quoted relative to the binding energy per atom in the stoichiometric compound. They include gains due to the symmetric relaxation of the nearest neighbors calculated via the pseudopotential method and an estimate of the elastic response of the crystal using the Keating model.[12] The lowest-energy defects are C_{Si} (1.1 eV), V_C (5.9 eV), V_{Si} (6.8 eV), and Si_C (7.3 eV). All the interstitial defects are significantly higher in energy. The high formation energy of Si interstitials was expected, due to the size differences between Si and C atoms and the small size of the tetrahedral interstitial cavity (0.94 Å) when compared to the covalent radius of the Si atom (1.18 Å).

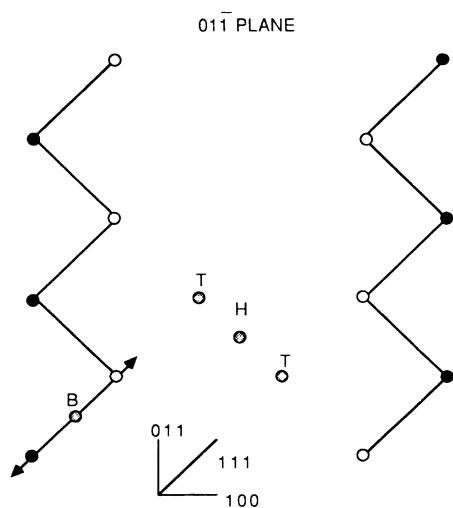In silicon, the formation energy of the Si self-interstitial

TABLE II. Formation energies for neutral T_d-symmetry point defects in stoichiometric cubic SiC.

	V_C	V_{Si}	Si_C	C_{Si}	Si_{TSi}	Si_{TC}	C_{TSi}	C_{TC}
E_f (eV)	5.9	6.8	7.3	1.1	15.0	14.7	8.6	11.0

is comparable to that of the vacancy,[13,14] while in diamond, which has a greater binding energy than SiC, the formation energy of the C interstitial is very high[11] (15–24 eV, depending on the atomic configuration). The very large formation energy of the C self-interstitial is due to its lack of low-lying d orbitals and the very high electron density and large band gap in diamond. In cubic SiC, where the electron density is lower and the band gap smaller, the formation energy of the C interstitial is lower. However, overcoordination is still not favorable for a carbon atom, since it does not have low-lying d orbitals.

The effects on the formation energy of atomic relaxations which maintain T_d symmetry vary, and to a large extent reflect the size differences between the carbon and silicon atoms. For example, the nearest-neighbor atoms around a carbon vacancy relax by 0.6% of the nearest-neighbor distance and the relaxation energy is negligible. By contrast, the relaxation of the atoms around a C_{Si} antisite defect is 8% inwards, and the relaxation energy is 0.7 eV. For the Si_C antisite, however, the nearest-neighbor atoms relax outwards by 12%, reducing the formation energy by 3.9 eV. The relaxation of the more distant neighbors, via the Keating model, contributed 0.3 eV to this last relaxation energy.

The concentrations of the various native defects in SiC are determined by their formation energies, subject to the constraint of a given deviation from stoichiometry (if any). Considering neutral defects for now, the dominant stoichiometry-preserving defect is the Si_C-C_{Si} antistructure pair (see Table II). Since the two antisites are nearest neighbors, the formation energy of the pair is reduced by its binding energy. Assuming the same relaxation distances of the nearest neighbors of the antistructure pair as in the case of isolated antisites, the formation energy of the pair is lowered to 5.9 eV from the 8.4 eV limit of two well-separated antisites. The corresponding V_{Si}-V_C divacancy has a formation energy of 8.1 eV.

The formation energy of a defect is also affected by its charge state, which in turn depends on the position of the Fermi level in the gap. In a system composed of a point defect and an electron reservoir with Fermi energy μ, the formation energy of a point defect in the charge state N is[4]

$$E_f(N,\mu) = E_f(N) - \mu N , \qquad (1)$$

where $E_f(N)$ is the formation energy of the defect calculated with respect to a fixed reference level (usually the top of the valence bands) and μ is the position of the Fermi level measured from this reference level. Note that the formation energy of a neutral defect is independent of the position of the Fermi level.

We have calculated the formation energies for the charged states of all eight elementary point defects listed

FIG. 1. Schematic view of the various native point defects which can exist in SiC. The T, H, and B denote the tetrahedral, hexagonal, and bond-centered sites of the interstitial. Note that in the SiC lattice two inequivalent sites exist for each of the point-defect types. Several of the point defects are accompanied by lattice distortions. See text.

in Table II, for the bond-centered interstitials and for the stoichiometry-preserving antistructure pair and the divacancy. It was found that the two point defects with the lowest formation energies in their neutral states, namely C_{Si} and V_C, remain the lowest-energy point defects for all Fermi-level positions. The divacancy formation energy is lowest in p-type material (6.9 eV), but it is still significantly higher than that of the neutral antistructure pair (5.9 eV). Similarly to the isolated antisites, the antistructure pair does not have any electronic levels in the gap. It is the lowest-energy defect in the perfectly stoichiometric SiC.

For the C-rich cubic SiC, the dominant defect is the C_{Si} antisite regardless of the position of the Fermi level. For Si-rich material, however, when one accounts for the fact that the Si_C antisite is twice as effective in compensating for excess Si atoms relative to the carbon vacancy, the nature of the dominant defect depends on the position of the Fermi level. In the intrinsic or n-type material, this defect is the Si_C antisite; for p-type material it is the carbon vacancy.

In Fig. 2 we plot the variation of the formation energy as a function of the Fermi level for the carbon vacancy. Although these results suffer from the well-known uncertainties associated with the use of local-density theory to determine band gaps and electronic excitations,[15] they show that the carbon vacancy is a double donor, regardless of stoichiometry. Both antisites, on the other hand, do not have electrically active levels in the gap and remain neutral regardless of the position of the Fermi level. From Table II and Fig. 2, the reaction $Si_C \rightarrow 2V_C^{2+}$ becomes exothermic in p-type material and the two electrons released during the reaction counteract the doping. Experimentally, strong self-compensation effects were observed in chemical-vapor-deposition-grown of Al-doped cubic SiC, where 40–60% of the acceptors were compensated. The doping efficiency of acceptors is also much lower than that of donors.[2,3]

Due to the large difference in electronegativity between Si and C atoms, the electronic structure of defects in SiC is similar to that of group III-V compounds, with the Si and C atoms acting in part as "cations" and "anions," respectively. For example, the Si dangling bonds of the carbon vacancy are relatively high in energy, making it a donor, while the C dangling bonds of the silicon vacancy are much lower and V_{Si} is an acceptor. In contrast to group III-V compounds, however, the antisites do not have electronic states in the forbidden gap.

As noted above, the present results show that the Si_C antisite is the dominant defect in the Si-rich intrinsic or n-type β-SiC, with the second most abundant defect being the carbon vacancy. They are consistent with experimental data, which show that "as-grown" cubic SiC is weakly n-type.[2] Furthermore, they are consistent with Birnie's[16] analysis of self-diffusion data, which suggested that C atoms diffuse via the carbon-vacancy mechanism, while Si atoms diffuse via Si_C antisites and carbon vacancies. Since lowering the Fermi level in Si-rich material results
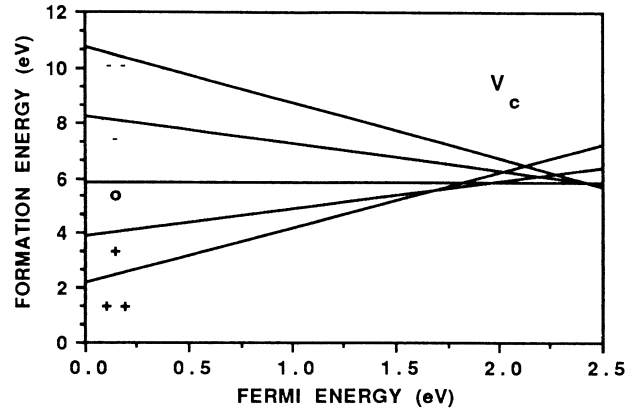

FIG. 2. The variation of the formation energy of the carbon vacancy as a function of Fermi-level position.

in the formation of carbon vacancies as the dominant stoichiometry-compensating defects, the doping efficiency of acceptors should be lower than that of donors, in agreement with experimental observations.[2,3] Considering other defects, all the tetrahedral and bond-centered interstitials we have studied act as donors, while the Si vacancy is an acceptor. In irradiated SiC, the Si vacancy and the interstitials will attract each other and annihilate, while the C vacancy is a donor and should be stable.

In summary, we have investigated the effects of deviations from stoichiometry on the relative abundances of native defects and on the electronic properties of cubic β-SiC. In a perfectly stoichiometric SiC, the dominant defect is the electrically inactive Si_C-C_{Si} antistructure pair. In Si-rich material the concentrations of the stoichiometry-compensating defects depend strongly on the Fermi-level position, with the Si_C antisite and the carbon vacancy being the dominant defects in n- and p-type material, respectively. Since the carbon vacancy is a double donor, it acts as a charge-compensating defect when the Fermi-level position is lowered and reduces the doping efficiency of acceptors. The electrically inactive C_{Si} antisite dominates in the C-rich material regardless of the position of the Fermi level. A slightly C-rich material is thus likely to be more suitable for electronic applications involving p-type SiC. Its hole mobilities should be substantially higher, due to a lower concentration of acceptors necessary to achieve a given concentration of holes. The feasibility of growing C-rich material has been recently demonstrated via molecular-beam-epitaxy techniques.[17]

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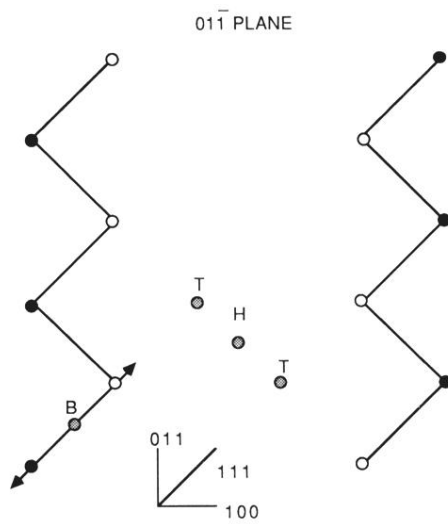
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