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Theoretical evidence for the kick-out mechanism for B diffusion in SiC

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In this letter, we analyze by means of first-principles electronic structure calculations the diffusion of B impurities in 3C-SiC. We find, through molecular dynamics, that substitutional B at a Si lattice site is readily displaced by a nearby Si interstitial by the process known as a *kick-out* mechanism, in agreement with recent experimental results. This is in contrast to the situation in Si, where B has recently been shown to diffuse via an interstitialcy mechanism. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1515369]

The diffusion of native defects and impurities in semiconductors is an issue of fundamental interest and great importance in the semiconductor industry. Notwithstanding this, there are still many open questions related to this topic.[1] There are several reasons for considering B diffusion in SiC. Firstly, SiC is at present the focus of considerable interest;[2] this material may succeed in overcoming the difficulties relating to temperature and voltage blocking of Si-based technology. Secondly, B is one of the p-type dopants most frequently used in SiC devices, particularly in the obtention of deep junctions for metal–oxide–semiconductor field effect transistor fabrication, and the ability to harness its diffusion in SiC could potentially be turned to advantage in the optimal design and fabrication of devices. In this letter we address the issue of B impurity diffusion in SiC by means of first-principles calculations. Our results clearly show that the process of B diffusion in this material is different than that found in Si. While no evidence is found for the kick-out mechanism of B diffusion in Si,[3] we conclude that it is the main mechanism of B diffusion activation in SiC. We present arguments based on the energetics of different configurations of the B impurity in 3C-SiC, and we confirm these arguments by direct first-principles molecular dynamics (FPMD) simulations. We believe that our conclusions on the likelihood of the kick-out mechanism also apply to hexagonal polytypes of SiC, because their structure, up to nearest-neighbor distances, is the same as that of 3C-SiC, although the actual diffusion of interstitial B (i.e., after the kick-out) may depend slightly on the polytype. Finally, we have identified the minimum energy path (MEP) for B diffusion through the interstitial region of SiC, finding a double-barrier path with an activation energy of ~0.65 eV.

The calculations described below have been carried out with the SIESTA[4] code, which implements density functional theory (DFT),[5] combined with the pseudopotential approximation and a basis set consisting of numerical atomic-like orbitals centered on the atoms. The pseudopotentials employed are of Troullier and Martins[6] type, in the separable form of Kleinman and Bylander.[7] We have used the local spin density approximation (LSDA)[8] of DFT for initial relaxations and FPMD simulations, though to compute the energy barrier to diffusion we have used the generalized gradients approximation (GGA).[9] A double-ζ plus polarization function basis set (DZP) was used for all the structural relaxation calculations, and four Monkhorst–Pack[10] k-points for the Brillouin zone sampling. For the FPMD simulations the DZP basis would be prohibitively expensive. We therefore designed a reduced basis set with smaller computational requirements, but still capable of providing good accuracy.[11] Tests on 3C-SiC using this methodology allow us to obtain a lattice parameter of 4.37 Å and a bulk modulus of 232 GPa, in good agreement with the plane-wave pseudopotential results of Chang and Cohen[12] (4.361 Å, 212 GPa) and Wang *et al.*[13] (4.36 Å, 235 GPa). The experimentally measured values[14] are 4.36 Å and 224 GPa, respectively.

We have analyzed a series of possible configurations for a B impurity in SiC. First, we have analyzed the substitutional configurations, where B lies in a Si or C site. It is well known[15] that, under appropriate values of the different chemical potentials involved, these sites are highly stable, and this stability is exploited in many microelectronic applications, where B is used as a shallow acceptor at a Si site.[16] Our results[11] reproduce this evidence, and confirm that substitution in the C sublattice is most favorable. However, in this work we focus on the analysis of the interaction of a B interstitial with the lattice, and of a B substitutional in the Si sublattice with the corresponding Si interstitial, in order to probe the possibility of intrinsic defect mediated diffusion. It has been experimentally demonstrated[17] that at typical annealing temperatures (~1700 °C) Fermi level effects on the diffusion of charged defects can be neglected, and therefore we did not take into account charged impurities in this work. The energetics of charged states is discussed elsewhere,[11,15] although we stress that these are not relevant for our present purposes. All configurations were fully relaxed using the conjugate gradients method.

The interstitial structure that turned out to be most stable under these conditions is the trigonal one (equivalent to the hexagonal in pure Si or diamond). All other relaxed structures are higher in energy; in particular the substitutional

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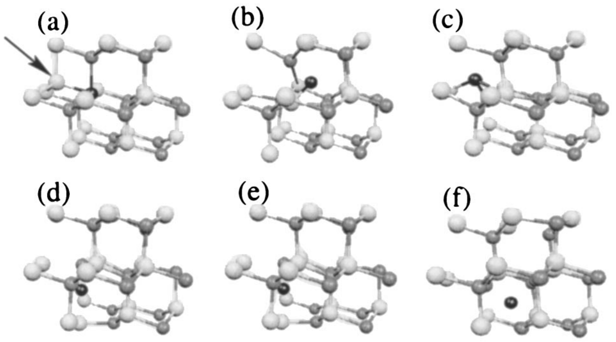

FIG. 1. Snapshots of the dynamics of a substitutional B impurity, illustrating the occurrence of the kick-out mechanism (see text). The arrow indicates the interstitial Si atom in its initial configuration. The large, light-gray atoms are Si, the smaller, dark-gray atoms are C, and the black atom is the B impurity.

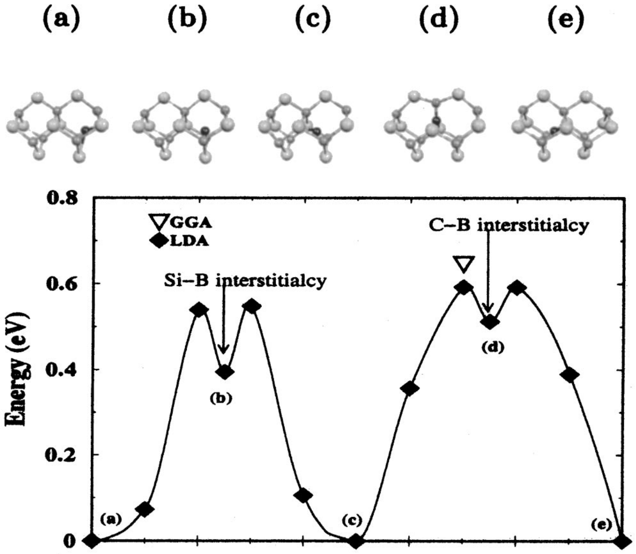

FIG. 2. Minimum energy profile for the diffusion of a B impurity between two equivalent trigonal sites. The snapshots illustrate the configuration of the impurity and nearby lattice atoms at representative points of the path. Configurations (a), (c), and (e) are trigonal interstitials, while (b) is a Si–B interstitialcy and (d) is a C–B interstitialcy.

configuration at a Si sublattice site coupled to a nearby Si interstitial, is 0.46 eV above the trigonal structure. This is at variance with the situation in Si, where the most stable configuration for B is substitutional, with a Si interstitial.[18] Thus the idea of a kick-out of substitutional B by a Si interstitial in Si is somewhat counterintuitive, given that, in this case, the substitutional site is the most stable one;[18] there is no driving force for the kick-out process to occur, and, should it occur, the impurity would rapidly kick in again. Indeed, recent simulations[3] find no evidence of a kick-out process for B diffusion in Si. However, as we have just seen, in SiC the situation is different. As argued earlier, substitutional B becomes metastable with respect to the trigonal interstitial structure in the presence of a Si interstitial, and therefore the kick-out process is energetically favorable. Prompted by this reasoning, we set out to perform a FPMD simulation to test the concept of the kick-out mechanism in SiC.

Newton's equations of motion were integrated numerically using Verlet's algorithm, with a time step of 2 fs, small enough to provide good energy conservation throughout the simulation. The total length of the run was 10 ps, and the initial velocities were sampled from the Maxwell–Boltzmann distribution at a temperature of 1000 K. The initial configuration consisted of a B substitutional impurity at a Si site, with the corresponding Si interstitial at a neighboring T_{Si} site [tetrahedral interstitial with four lattice Si atoms as nearest neighbors, [see Fig. 1(a)]. The Si interstitial very rapidly jumps from the interstitial site; likewise, the B atom moves out of the lattice site, although its displacement is initially smaller. The displacement of the Si atom is in the direction of the lattice site, where it settles after the first 0.5 ps of the simulation, as can be appreciated in Figs. 1(a) and 1(b). The impurity, however, moves more slowly, and during the first ps it forms an interstitialcy complex with the Si atom [Figs. 1(b)–(d)] now occupying that site (the former interstitial). After 1 ps the interstitialcy dissociates $(1e)$, leaving the Si atom at the lattice site, and the B impurity migrates to a nearby trigonal interstitial position $(1f)$, where it remains for the rest of the time spanned by the simulation.

Recently, Bracht *et al.*[17] have interpreted their experimental results on B diffusion in 4H- and 6H-SiC in terms of the kick-out mechanism. The alternative dissociative mechanism, in which a B substitutional impurity dissociates into a vacancy and a B interstitial, could not account for the observed depth concentration profiles, while the kick-out mechanism provided an accurate fit to the data. Our results, which clearly show the occurrence of the kick-out mechanism, do lend more weight to the conclusion reached by Bracht and coworkers. Another piece of experimental evidence fitting in this argument is the work of Janson *et al.*,[19] where it is found that B diffuses up to two orders of magnitude faster in implanted 4H-SiC than in equilibrium conditions, implying that B diffusion is a transient enhanced process. Our results clearly show that the presence of native interstitials, facilitated by the implantation process, can easily induce the kick-out of B into the interstitial space, through which it can diffuse. However, the FPMD simulation is too short to span a time scale long enough to monitor the process of B diffusion directly. An alternative in these cases can be the location of MEPs, which illustrate the diffusion mechanism and provide the energy barriers to the process. Here we have used a method consisting of a series of constrained relaxations, restricting the B atom to lie in a plane perpendicular to the diffusion path. The constraining plane is moved in a series of steps along the diffusion path, and at each step a full relaxation of the whole system is carried out, imposing only the condition that the impurity remains within the constraining plane. The MEP obtained is rather straight, physically plausible, and contains no suspect discontinuities. Once the MEP was obtained, the highest and lowest energy points along the path were relaxed again using GGA[9] and spin polarization to obtain a more accurate estimation of the barrier height. The MEP we have found is illustrated in Fig. 2; it maps out the path followed by a B impurity after it has been kicked out to a trigonal interstitial position. As can be seen in Fig. 2, the path goes through two double barriers of slightly different heights. In the middle of each barrier an interstitialcy complex is formed that is a local minimum. In the first barrier, the interstitialcy consists of the B impurity paired up with a Si lattice atom [Fig. 2(b)], which is slightly more stable than the interstitialcy formed with a C atom [Fig. 2(d)]. In between both barriers, another trigonal interstitial configuration is found. We emphasize that the barrier reported in Fig. 2 is not the total energy barrier for B diffusion in SiC, which should also account for the diffusion of Si interstitials and the kick-out process itself, and which has been recently measured experimentally to be 4.7 ± 0.5 eV,[20] but only the barrier experienced by B once it has been kicked out. The interstitial diffusion of the B impurity will continue until it encounters a vacancy site, where it will form a highly stable substitutional impurity, or until it meets the surface.[17,19]

In summary, we have found evidence in support of a kick-out process as the main activation channel of B diffusion in SiC at high temperatures. We have performed a FPMD study starting from a B substitutional impurity at a Si site near a Si interstitial, and our trajectory shows clear evidence for the kick-out mechanism, in contrast to what happens in Si, where B has been shown to diffuse through an interstitialcy mechanism.[3] We have also determined the MEP for B diffusion in SiC, from which we can conclude that B diffuses from trigonal site to trigonal site via C and Si interstitialcies. The highest barrier to be overcome along this path is 0.65 eV according to GGA calculations, occurring near the B–C interstitialcy, although the total effective barrier should be larger, since other processes such as Si interstitial diffusion also contribute to the latter.

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