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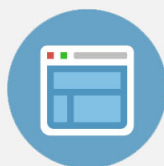
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First-principles study of *n*-type dopants and their clustering in SiC

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We report the results of an *ab initio* study of N and P dopants in SiC. We find that while N substitutes most favorably at a C lattice site, P does so preferably at a Si site, except in *n*-doping and Si-rich 3C-SiC. Furthermore, we consider a series of dopant complexes that could form in high-dose implantation, in order to investigate the dopant activation behavior in this limit. We find that all N complexes considered lead to passivation through the formation of a deep level. For P, the most stable aggregate is still an active dopant, while passivation is only observed for complexes with a higher formation energy. We discuss how these results could help in the understanding of the observed experimental high-dose doping and codoping behavior of these species. © 2003 American Institute of Physics. [DOI: 10.1063/1.1583870]

In recent years, interest in SiC as a material for applications in the semiconductor industry has been steadily growing, given its advantages over Si under conditions of high power, high temperature, and radiation. Nitrogen and phosphorus are the most commonly used *n*-type dopants in applications of SiC. Since ion implantation is the only viable way to dope SiC, N has the considerable advantage of a low mass, which makes it the most typical choice as a donor species. On the other hand, P has a higher solubility limit in the SiC lattice and a higher electron mobility at high doses with respect to N. Electron-spin resonance experiments indicate that N is most favorably substituted at a C sublattice site,¹ while P is most likely to substitute at a Si sublattice site.² This fact, together with the observation that N and P donors have similar ionization energies,³ suggested that codoping of SiC with both N and P could maximize the doping efficiency, resulting in an overall increase in the dopant activation rate. Laube *et al.*⁴ have reported comparative Hall effect measurements implanting N and P, and co-implanting the two at three different doses. At the highest dose ($\approx 2.4 \times 10^{20} \text{ cm}^{-3}$), implanting P alone provided the most effective doping, followed by co-implanted N and P, and then by N alone. Further studies on N/P co-implantation have been carried out by other groups,⁵ focusing on the benefit of co-doping from the viewpoint of the annealing of the damaged layer. On the theoretical side, N in SiC has been studied by means of first-principles calculations by different groups,^{6,7} P-related complexes and the deep levels they induce have been analyzed by Gali *et al.*,⁸ but a comprehensive study of its stability at different lattice sites in 3C and 4H-SiC has not yet been carried out.

In this work, we report a theoretical study based on first-principles electronic structure calculations, addressing the structural and doping properties of N and P in the 3C and 4H polytypes of SiC. The aim of this work is to establish theo-

retically the preferred substitutional sites of both N and P in SiC under different stoichiometry and doping conditions. Furthermore, we also investigate the effects of high-dose implantation of N and P, discuss the likely implications for codoping, and advance a possible explanation for the lower-than-expected efficiency of high-dose implantation of N. Our calculations were performed using the SIESTA⁹ package, which implements density functional theory¹⁰ with the pseudopotential approximation and a basis set consisting of atomic-like numerical orbitals. We used nonlocal Troullier–Martins¹¹ pseudopotentials¹² and the local density approximation.¹³ The single-particle orbitals were represented using a double- ζ basis set with energy shift 0.025 eV;⁹ we have shown in our recent work,¹⁴ that this basis is sufficiently flexible to reproduce the structural parameters and bulk modulus of 3C-SiC with great accuracy. In our calculations, the simulation cells contained 64 atoms in the case of 3C-SiC, and 96 in the case of the 4H polytype; in both cases, a set of four *k*-points generated according to the Monkhorst–Pack¹⁵ scheme was used to sample the Brillouin zone. In the case of charged dopants, we have used the Madelung correction described by Makov and Payne.¹⁶ The formation energies of the different defects considered have been calculated using the formalism of Northrup and Zhang,¹⁷ and are given as a function of the electron chemical potential and the C-Si chemical potential difference (μ_e and $\Delta\mu$, respectively). In principle, one needs to define also a chemical potential for the impurity, but this is made difficult by the need to take an appropriate reference state (details on how it can be done in the case of H can be found in Ref. 18). We have avoided this difficulty by following the procedure of Fukumoto,¹⁹ where, by always comparing systems with the same numbers of dopants, the chemical potential of the dopant is canceled out.

Let us now move on to discuss the relative stabilities of N and P in different charge states at the different lattice sites. We first consider the case of N in 3C-SiC. We find that the

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substitutional N at a C site, that is, the N(C) substitutional, preserves the tetragonal symmetry of the C site. However, a N atom at a Si lattice site relaxes to an off-center position, which is $\sim 0.4 \text{ \AA}$ from the perfect lattice Si site, lengthening the bond to one of the nearest neighbors and shortening the remaining three bonds, in agreement with previous results.^{6,7}

We predict that a N substitutional is most stable by far at a N(C) site; the energy difference between the N(Si) and N(C) is approximately 6 eV throughout the range of doping conditions. That the N(C) configuration is energetically more favorable is in agreement with experimental observations, but the difference of formation energies for N(Si) and N(C) configurations is larger than that obtained in the previous theoretical study of Miyajima *et al.*⁶ The origin for this discrepancy may be attributed to the different approximations used in Ref. 6, although a rigorous analysis is not possible since details of their calculations were not given. As expected, the most stable charge state of the dopant at zero temperature depends on the position of the electron chemical potential μ_e . When μ_e is below the doping level, the charge state is $+1$, while n -doping conditions lead to a neutral state.

The case of P deserves closer attention, due to the fact that the experimental situation is far less clear than that of N. In the case of 3C-SiC, the results of our study indicate that P is most favorably located at a Si sublattice site: P(Si). In both substitutional sites, the P atom retains the perfect lattice symmetry. The formation energy difference between P(C) and P(Si) is significantly smaller than in the case of N, and its value depends on the charge state of the dopant. For the $+1$ state, the energy difference is 0.68 eV. For the neutral state, the difference is reduced to 0.24 eV. Given that the energy differences between different dopant configurations of P in 3C-SiC are much smaller than for N, we have also considered its stability behavior in 4H-SiC. In the 4H polytype, there are four inequivalent positions (since both Si and C can take either cubic or hexagonal lattice sites) where P can substitute. However, the difference of stability for P substituting a given host species at a cubic or hexagonal site is only of the order of hundredths of an eV. Once again, P(Si) is more stable than P(C) for all the doping conditions of the host material, the energy difference varying from 0.55 to 0.73 eV, depending on the value of μ_e . As in the case of 3C-SiC, at zero temperature P is found in the $+1$ (0) charge state for μ_e below (above) the dopant state.

The results discussed so far have been obtained assuming the condition of perfect stoichiometry; that is, $\Delta\mu = 0$. We have also considered the two limiting cases of Si-rich and C-rich material. In the Si-rich case, the substitution of a dopant at a C site is $\frac{1}{2}H_f$ more stable with respect to the stoichiometric case, where $H_f \approx 0.4 \text{ eV}$ is the SiC formation heat; in the same way, substitution at the Si site is $\frac{1}{2}H_f$ less stable; the overall result is that the difference in stability between a dopant at a Si site and the same atom at a C site is lowered by an amount of H_f . For C-rich material, the opposite is the case, so that the substitution at the Si site is made more stable. These considerations are not very important for N, where the difference between the formation energy of N(Si) and N(C) is one order of magnitude larger than H_f . However, they become more relevant in the case of P, where P(C) can even be made slightly more stable than P(Si) in

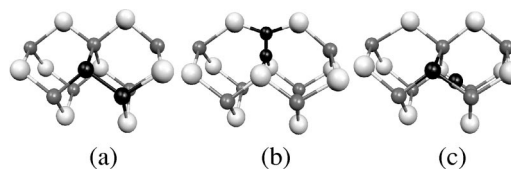


FIG. 1. Impurity aggregates (before relaxation) selected to model the high-dose condition. Light-gray balls are Si atoms, dark-gray balls are C atoms, and black balls represent the dopant atoms. (a) Substitutional dimer at nearest neighbor lattice sites; (b) split interstitial (in this particular case at a C site); (c) substitutional plus interstitial.

3C-SiC (but not in 4H-SiC), when conditions of n -type doping and of Si-rich material hold simultaneously. In agreement with published experimental results,^{1,2} our calculations allow us to conclude that, in a SiC lattice, a N atom will substitute most favorably at a C site, while a P atom will do so at a Si lattice site, although in the latter case the preference can be reversed in 3C-SiC in the conditions discussed earlier.

We have analyzed a few dopant aggregates in 3C-SiC that can possibly form during the implantation cascade, in search for some passivation effect responsible for the low activation of N at high doses,⁴ which appears to be the dominant bottleneck. The configurations that we have taken into account are shown in Fig. 1, and are first-neighbor substitutionals, split interstitials, and substitutional plus interstitial. Malhan *et al.*²⁰ have used a similar approach to investigate second-nearest-neighbor aggregates. These complexes are intended to model representative situations, ranging from the efficient occupation of neighboring sites (first neighbors substitutionals) to site sharing (split interstitials at the favored site). First, we have calculated the aggregation energy E_{agg} ²¹ of these compounds with respect to the most stable arrangement for each species [P(Si) and N(C)], and we have found out that none of them would form spontaneously in thermal equilibrium ($E_{\text{agg}} > 0$, ranging from 0.3 to 3 eV). Therefore, they can only be a product of the nonequilibrium conditions that the material experiences during the implantation cascade. However, all the configurations are stable in the sense that, once they have formed, an energy barrier must be overcome to dissociate them.

In the case of N aggregates, the identity of the lowest energy complex depends on the value of the chemical potential μ_e . However, in all cases, we find that the two N atoms mutually passivate, as can be clearly seen in Figs. 2(e) and 2(f), which show the band structure of the substitutional dimer and of the split interstitial. In the case of P, the most stable aggregate (by as much as 3 eV) regardless of the value of μ_e and $\Delta\mu$, is the first-neighbor P substitutional, which does not show self-passivation behavior [Fig. 2(d)]. This is in contrast to the situation of the N first-neighbor substitutional, which does [Fig. 2(e)]. In the latter case, there is an appreciable off-center relaxation of the N at the Si site, which leads to a deep state in the gap. The presence of a second N at a nearest-neighbor site further increases the depth of the dopant state, which is now fully occupied. On the other hand, in the case of the split-interstitial, the fully occupied state near the middle of the gap generates from the π molecular states of the N_2 molecule, whose formation is allowed by the short interatomic distance to which the two N relax. Our calculations are certainly not capable of giving an

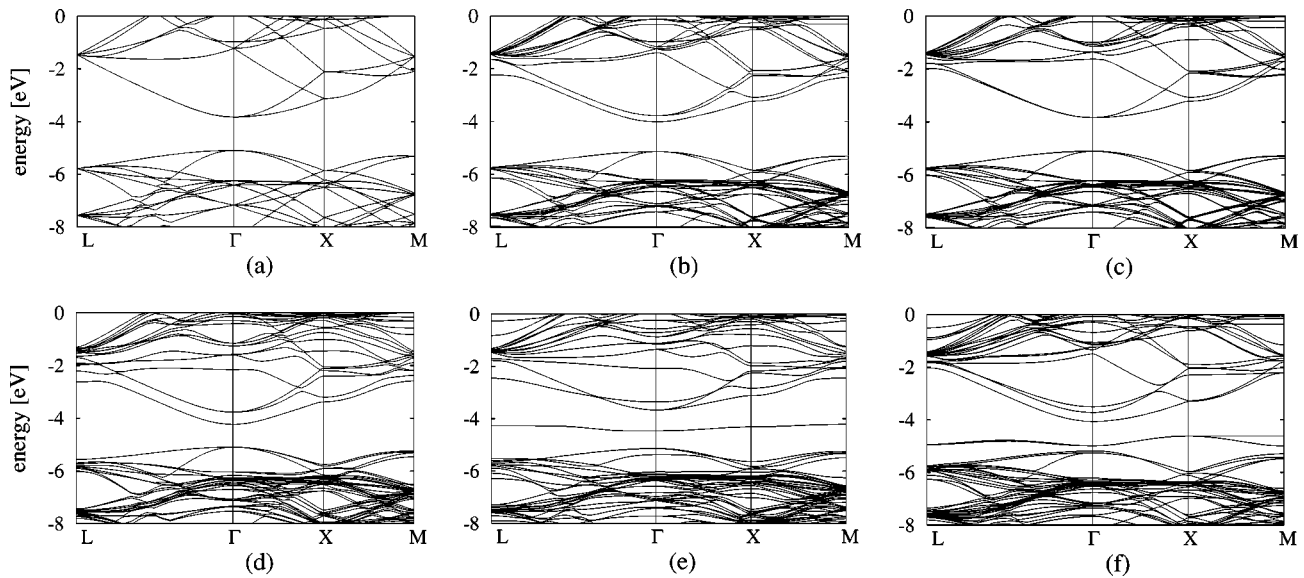


FIG. 2. Band structure of the 64-atom cubic supercell of 3C-SiC. (a) Impurity-free host crystal. (b) Supercell containing a N at a C site. (c) Supercell containing a P at a Si site. (d) Supercell containing a P substitutional dimer at first neighbor sites. (e) Supercell containing a N substitutional dimer at first neighbor sites. (f) Supercell containing a nitrogen split interstitial.

accurate estimate of the position of the shallow states within the band gap, due to the small size of the supercells compared to the spread of the doping states. However, Fig. 2 gives a clear indication that N aggregates have a tendency to form a passivated state, while P, in its most stable configuration, does not. We propose that self-passivation may be one of the main channels through which the N activation rate decreases with the implanted doses.

We have also investigated the case of the mixed N and P aggregate, namely, a substitutional dimer with P(Si) and N(C). A passivation effect shows up in this case as well, even if it is less pronounced than in the case of all-N aggregates. This may be another relevant channel for dopant passivation at high doses and should also affect P, but further investigation is needed in this direction to completely clarify this issue.

To summarize, we have established from first principles that in SiC *n*-type dopants N and P substitute preferably at C and Si lattice sites, respectively, and this trend is manifested in equal measure in both the 3C and 4H polytypes. We have also analyzed a series of dopant aggregates that could form during high-dose implantation, finding that all investigated N complexes lead to a self-passivation effect, which could account for the low efficiency of high-dose N implantation. Of the P aggregates considered, the energetically most favorable one among those investigated does not suffer from any such self-passivation effect. This could explain the higher efficiency of P-doped SiC in the high-dose implantation limit.

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- ²¹The aggregation energy can be conveniently defined, for instance, in the case of P, as $E_{\text{aggr}} = E_{\text{form}}[P_2] - 2E_{\text{form}}[P(\text{Si})]$, where P_2 is any complex involving two P atoms, and $P(\text{Si})$ is the reference configuration for an isolated P dopant.