# Shallow Donors in Diamond: Chalcogens, Pnictogens, and their Hydrogen Complexes

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The utility of diamond as an electronic material is compromised by the lack of a suitable shallow donor. Here, *ab initio* theory is used to investigate the donor levels of substitutional pnictogen (N, P, As, and Sb) and chalcogen (S, Se, and Te) impurities and chalcogen-hydrogen defects in diamond. Substitutional S is found to be a deep donor, while As and Sb possess donor levels significantly shallower than P, which so far is the most effective shallow donor found by experiment.

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Diamond represents a material with great potential for use as a semiconductor in applications that require high-frequency, high-temperature, high-power, and high-irradiation-tolerant devices [1]. These desirable properties are due to diamond's high carrier mobility, high thermal conductivity, high breakdown field, low dielectric constant, and wide band gap. The creation of such devices requires the fabrication of low-resistivity *n*- and *p*-type material by doping diamond with donor and acceptor impurities, respectively. Boron has been successfully both grown into and implanted into diamond, and forms *p*-type layers with a resulting activation energy of 0.38 eV. However, it has proved difficult to find a shallow donor for the production of *n*-type material. The most successful dopant to date is substitutional phosphorus.

Phosphorus can be grown into chemical-vapor deposited (CVD) diamond in significant doping concentrations ($\sim 10^{18}$ cm$^{-3}$), mainly on substitutional sites (P*s*) [2]. This greatly exceeds the solubility expected from the high bulk formation energy of ~7–11 eV found by theory [3–5]. This large value results from the covalent bond radius of P (106 pm) being significantly greater than that of C (77 pm). However, the high concentration of $P_s$ is only found in $\langle 111 \rangle$ sectors, which suggests that the supersaturation arises from an effective incorporation at the growing surface. The important implication is that other dopants with large covalent radii might also be grown in supersaturation conditions into diamond via a similar mechanism.

Substitutional nitrogen ($N_s$) has high solubility in diamond and has a low formation energy [4,5]. However, $N_s$ acts as a very deep donor, with an observed activation energy of around 1.6–1.7 eV [6–8].

There have been several suggestions for shallow donors [4,9,10]. These include S, S–H and more complex defects such as $N_2$–H [10]. The last is unlikely to be found in CVD diamond while the energy levels of the former are controversial. This investigation contributes to this debate and continues the search for shallow donor impurities in diamond by considering other chalcogens Se and Te as well as pnictogens As and Sb. N and P are also examined for reference to earlier work. The motivation for examining the other chalcogens and pnictogens follows from similar studies in silicon. Here it is known that the donor level of $Sb_s$ at 0.039 eV below the conduction band minimum energy $E_c$ is shallower than that of $P_s$ ($E_c - 0.045$ eV) [11]. In addition, although $S_s$, $Se_s$, and $Te_s$ introduce deep single and double donor levels, their singly hydrogenated complexes possess donor levels much shallower than the isolated atom [12]. Such defects have been studied by electron-nuclear double resonance [13,14], Fourier-transform infrared (FTIR) spectroscopy [15], deep-level transient spectroscopy [16,17], and time-dependent conversion electron Mössbauer spectroscopy [18]. The FTIR data, in particular, reveal a number of shallow donors associated with $S_s$–H having levels around 0.1 eV [15]. The role of hydrogen in *diamond* has recently received much attention in theoretical work [19].

Local spin-density-functional-theory (DFT) calculations were carried out using the AIMPRO software [20,21]. They were performed in 64- and 216-atom cubic supercells of diamond into which a substitutional impurity atom was placed, along with a hydrogen atom when investigating impurity-hydrogen complexes. Each system was allowed to undergo a full structural relaxation at fixed volume, both with and without constraints on the symmetry of the defect where appropriate.

The atoms are treated using the pseudopotentials of Hartwigsen, Goedecker, and Hutter [22]. The basis sets used consisted of *s*, *p*, and *d* Gaussian orbital functions centered at the atomic sites with four or five exponents. Calculations were carried out using a set of eight (MP-$2^3$) special **k** points to sample the band structure. The charge density is Fourier transformed using plane waves with an energy cutoff of 300 Ry. The use of this basis set in a 64-atom supercell leads to a diamond lattice constant of 3.53 Å and a bulk modulus of 465.8 GPa, values 99% and

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105% of the standard experimental results, respectively. The direct band gap for this setup is 5.57 eV, and the indirect gap is 4.22 eV, these being, respectively, 98% and 101% of previously published theoretical values [23].

Each substitutional defect atom $X_s$ was investigated in two positions: (i) $X_{\mathrm{latt}}$, where the $X_s$ atom lies perfectly on a lattice site and the $T_d$ symmetry of the system is maintained; (ii) $X_{\mathrm{shift}}$, where $X_s$ is slightly shifted from the lattice site in $[\bar{1}\,\bar{1}\,\bar{1}]$, resulting in a system with $C_{3v}$ symmetry. Those defects that were found to be more stable when shifted from the lattice site were also modeled with an initial shift in [110], although in all cases the final structure took on the same form and energy as that found for the $[\bar{1}\,\bar{1}\,\bar{1}]$-shift calculation.

Three sites for hydrogen bound with $X_s$ were investigated. These were: (i) $X_s$–$\mathrm{H}_{\mathrm{bc}}$(bond centered), where the H atom is at the center of the bond between the defect $X_s$ and the nearest C atom in [111], such that there is a $X_s$–H–C axis; (ii) $X_s$–$\mathrm{H}_{\mathrm{ab}}$ ($X_s$ antibonding), where the H atom lies behind the impurity atom in $[\bar{1}\,\bar{1}\,\bar{1}]$, such that there is a H–$X_s$–C axis; (iii) $X_s$–$\mathrm{H}_{\mathrm{ab}}^{\mathrm{C}}$(C antibonding), where the H atom resides behind the [111] C neighbor to the impurity, such that there is a $X_s$–C–H axis. These sites are summarized in Fig. 1. These complexes all have $C_{3v}$ symmetry.

There are at present several methods for calculating the electrical energy levels of defects, none of which has become universally accepted. The *formation energy method* (FEM) involves comparison of the calculated formation energies of defects in different charge states, and is discussed fully in Ref. [24]. The *marker method* was employed in this investigation and proceeds as follows. Each system is modeled in the neutral charge state $X_s^0$ and with an electron removed $X_s^+$, so that a characteristic "ionization" energy $E(0/+)_X = E(0)_X - E(+)_X$ can be calculated as the difference between the final energy of the neutral system $E(0)_X$ and the final energy of the system in the positive charge state $E(+)_X$. We compare this $E(0/+)_X$ with the $E(0/+)$ calculated for a standard defect whose electrical level is well known (the *marker*), in order to infer the level of $X$ [25–27]. This method eliminates systematic errors in DFT calculations where an underestimate in the band gap may significantly perturb the position of the defect levels, and where systematic errors come from the compensating background present for charged defects [28]. The method has been used with great success in the case of chalcogen defects in silicon, where it corrected errors of the order of 0.5 eV encountered when using the FEM [12].

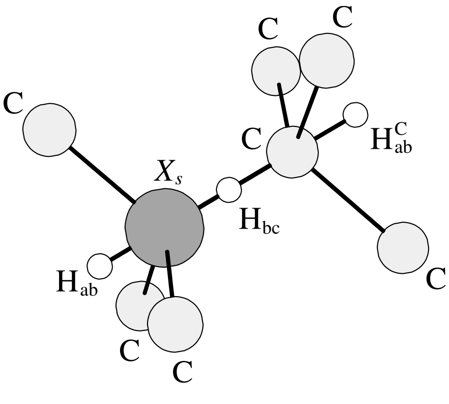

FIG. 1. Sites for the H atom in defect-hydrogen complexes in diamond. The substitutional defect $X_s$ is shown in dark gray, while C and H atoms are light gray and white, respectively. The H atom is shown in three positions: Antibonded to the defect, $\mathrm{H}_{\mathrm{ab}}$; Antibonded to a C neighbor of the defect, $\mathrm{H}_{\mathrm{ab}}^{\mathrm{C}}$; At the middle of a $X_s$–C bond, $\mathrm{H}_{\mathrm{bc}}$.

Substitutional phosphorus was used as the marker in the present calculations, i.e., we compare the defect ionization energy $E(0/+)_X$ with that found for substitutional phosphorus, $E(0/+)_{\mathrm{P}}$. The donor level of the defect below the conduction band is then given by $D_X = D_{\mathrm{P}} + E(0/+)_{\mathrm{P}} - E(0/+)_X$, where the donor level of phosphorus, $D_{\mathrm{P}}$, is taken from experiment. The donor levels of defects presented in this Letter are therefore found via *shifts from the phosphorus donor level.* Phosphorus in diamond was originally assigned a donor level around $E_c - 0.4$ eV [29], although several, more recent measurements place it ~0.6 eV below $E_c$ [30–34]. This value is much lower than the 0.218 eV expected from the effective-mass approximation (EMA) [34], suggesting a large repulsive central potential.

A number of tests are required in our calculations in order to check that the energy is converged sufficiently with respect to the values of several parameters. The density of the **k**-point sampling mesh was investigated for both 64- and 216-atom supercells, each containing a single substitutional antimony atom on a lattice site—antimony being the largest atom under investigation and therefore potentially the most disruptive to the lattice. Total energies were converged to 10 meV for a **k**-point sampling of MP-$2^3$. The convergence of energies with respect to the value of the plane-wave cutoff energy $E_{\mathrm{cut}}$ was investigated in the same supercells. Total energies $E(0)_{\mathrm{Sb}}$ and $E(+)_{\mathrm{Sb}}$ were converged to 10 meV for $E_{\mathrm{cut}} \gtrsim 300$ Ry, while energy differences $E(0/+)_{\mathrm{Sb}}$ were sufficiently converged even for very low values of $E_{\mathrm{cut}}$. Unless otherwise stated, values in this Letter are presented based on calculations performed in the 216-atom supercell.

We find that the tetrahedral defect $\mathrm{P}_{\mathrm{latt}}$ and the trigonal defect $\mathrm{P}_{\mathrm{shift}}$ possess very similar energies. In the latter case, the unique $\mathrm{P}_s$–C bond is 9.6% longer than a normal C–C bond in diamond, while the other three $\mathrm{P}_s$–C bonds are extended by 10.4%. This represents an average 10.2% extension over a normal C–C bond. The reorientation barrier among the four equivalent trigonal structures was calculated in the 64-atom supercell to be ~70 meV. The $C_{3v}$ symmetry is consistent with recent electron spin resonance studies [35].

In agreement with previous studies [3,9,36], the trigonal $\mathrm{S}_{\mathrm{shift}}$ sulfur defect was most stable—the $\mathrm{S}_{\mathrm{shift}}$ center was over 0.5 eV lower in energy than the on-site $\mathrm{S}_{\mathrm{latt}}$ when neutral. The ionization energy for $S_{\text{shift}}$ was found to be 0.8 eV lower than the reference ionization energy calculated for $P_s$, and so, with the use of our empirical $P_s$ donor level of $E_c - 0.6$ eV, the $S_{\text{shift}}$ donor level is given as $E_c - 1.4$ eV. This is close to a previous estimate [9]. Experimentally, initial claims of shallow donor behavior due to S have more recently been attributed to *p*-type conduction due to contamination by boron [37]. The structures of $Se_s$ and $Te_s$ are similar to $S_s$, while we find that their donor levels are also deep and lie at $E_c - 1.4$ eV and $E_c - 1.2$ eV, respectively.

Turning to the singly hydrogenated chalcogen centers, the most stable configuration for the $S_s$–H complex was $S_s$–$H_{\text{ab}}$, which was ~1–2 eV lower in energy than the $S_s$–$H_{\text{ab}}^{\text{C}}$ and $S_s$–$H_{\text{bc}}$ configurations. The donor level for the $S_s$–$H_{\text{ab}}$ complex is calculated to be at $E_c - 1.0$ eV. When compared with $E_c - 1.4$ eV for the unhydrogenated $S_{\text{shift}}$ substitutional, we see that the presence of antibonding hydrogen makes the defect noticeably (0.4 eV) shallower. This is in line with previous studies placing the donor at $E_c - 1.07$ eV [38], and with the corresponding defects in silicon.

The $Se_s$–$H_{\text{ab}}^{\text{C}}$ and $Se_s$–$H_{\text{ab}}$ complexes were found to be energetically equivalent in the neutral charge state, while in the positive charge state, $Se_s$–$H_{\text{ab}}^{\text{C}}$ is ~0.1 eV more stable than $Se_s$–$H_{\text{ab}}$. The calculated donor level for $Se_s$–$H_{\text{ab}}^{\text{C}}$ lies at $E_c - 0.9$ eV, slightly nearer the donor level of phosphorus than that of the most stable $S_s$–H complex. A hydrogen atom has made the isolated $Se_s$ defect a shallower donor by 0.5 eV.

$Te_s$–$H_{\text{ab}}^{\text{C}}$ was found to be the most stable $Te_s$–H complex. This was the only hydrogen complex under investigation to have a donor level comparable with that of substitutional phosphorus. $Te_s$–$H_{\text{ab}}^{\text{C}}$ has a donor level calculated in the 64-atom supercell to lie at $E_c - 0.5$ eV, while the 216-atom supercell calculations place this at $E_c - 0.7$ eV. It is to be concluded that $Te_s$–$H_{\text{ab}}^{\text{C}}$ represents a donor with a level approximately the same as that of $P_s$.

We now turn to substitutional pnictogen defects. The trigonal $N_{\text{shift}}$ defect was found to be over 0.5 eV more stable than $N_{\text{latt}}$ when neutral, in agreement with previous theoretical studies [4,39,40], and consistent with the properties of the "P1" EPR center attributed to substitutional N [41,42]. The $N_{\text{shift}}^0$ atom moves farther away from the lattice site in the $[\bar{1}\,\bar{1}\,\bar{1}]$ direction, breaking the unique $N_s$–$C_{[111]}$ bond by increasing it to 129.2% of a normal C–C bond length. The three $N_s$–C bonds became 95.6% of the normal C–C length. Conversely, the positively charged $N_{\text{shift}}^+$ was stable on the lattice site, all $N_s$–C bonds being fully relaxed and equal in length at 100.7% of that of a normal C–C bond. This is the well-documented chemical rebonding sometimes referred to as the "pseudo-Jahn-Teller" effect. The $N_s$ atom prefers to be threefold rather than fourfold coordinated, and its remaining two electrons occupy a lone-pair orbital directed toward a *p*-dangling bond on a $C_{[111]}$ atom. As this dangling bond contains an electron, there is an interatomic repulsion arising from the Pauli principle, and the $N_s$ and $C_{[111]}$ atoms mutually move apart. The donor level found by comparing the energies of the two charge states of the $N_s$ defect lies at $E_c - 1.7$ eV. Other *ab initio* work [38] calculates the $N_s$ donor level to lie 1.92 eV below the conduction band minimum, while the substitutional nitrogen activation energy has been experimentally measured in diamond films to be $1.62 \pm 0.02$ eV [6], 1.7 eV [8], and is 1.7 eV in amorphous tetrahedral carbon [7]. The very good agreement with this known donor level gives confidence in the method used in this work.

The behavior of $As_s$ is very different from $N_s$. The $As_{\text{latt}}$ and $As_{\text{shift}}$ forms differed in structural energy by an insignificant amount in both charge states. $As_{\text{shift}}$ was observed to move back onto the lattice site in both charge states, and the C atoms surrounding the $As_s$ were equally displaced outward, giving rise to a center with $T_d$ symmetry. When neutral, the final $As_s$–C bonds were 114.8% of a normal C–C bond length. Although these bonds are longer than those of carbon, they are comparable with those of $Ni_s$–C which can occur in large concentrations of around 60–70 ppm [43]. Implantation experiments [44,45] have shown that about half of all implanted As atoms lie at substitutional sites, but the electrical properties are unknown.

The donor level for $As_{\text{latt}}$ lies at $E_c - 0.3$ eV and at $E_c - 0.4$ eV in the 64- and 216-atom supercells, respectively, and we can conclude that substitutional As centers will require a donor activation energy of ~0.4 eV. This represents a donor that is unambiguously shallower than substitutional phosphorus. We have calculated the electronic band structures in 216-atom supercells for the three cases of: pure bulk diamond; diamond with $As_s$; diamond with $P_s$, and a comparison of the energy bands is shown in Fig. 2. Indeed, we notice that the highest occupied band for the defect is closer to the bulk diamond conduction band states than the corresponding $P_s$ defect band, systematically throughout $\mathbf{k}$ space.

Similarly to arsenic, the structures $Sb_{\text{latt}}$ and $Sb_{\text{shift}}$ are energetically equivalent in both charge states, and in all cases $Sb_{\text{shift}}$ moved back onto the lattice site. Substitutional antimony is predicted to be a very shallow donor indeed, with a calculated level at $E_c - 0.2$ eV in the 64-atom supercell, very close to the EMA, and at $E_c - 0.3$ eV in the 216-atom supercell. Now, Sb is a very large atom (with a covalent radius of 138 pm), and the $Sb_s$–C bonds are 22% longer than C–C bonds. However, this strain is very local, as second-neighbor C–C bonds are shortened by only 2%.

We have also investigated the complexes of pnictogens with H, but in every case they produced only very deep donor levels, in agreement with previous studies on N–H and P–H defects [5].

In conclusion, we have found that substitutional arsenic and antimony possess significantly shallower donor levels in diamond and lie closer to the effective-mass value of $E_c - 0.218$ eV than substitutional phosphorus.

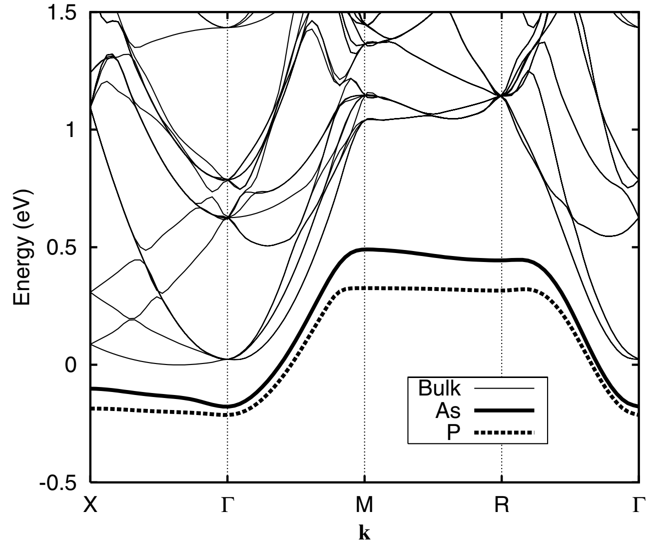

FIG. 2. Band structure diagram showing the highest occupied electronic bands for As and P substitutional defects, together with the conduction band states for defect-free bulk diamond. The three band structures have been aligned by their valence band maxima at the Γ point. The zero of the energy scale corresponds to the bulk diamond conduction band minimum.

We believe that the solubilities of the chalcogens and pnictogens are likely to be negligible but that they may be introduced, as in the case of $P_s$, by favorable surface chemistry. However, it is possible that donor activity is compensated by the formation of defects such as impurity-vacancy centers.

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