Nitrogen and Potential *n*-Type Dopants in Diamond

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Potential *n*-type dopants in diamond are investigated via *ab initio* methods. The well-known distortions around the deep donor N are found to arise from the interaction of the N lone pair with a C dangling bond. P, Li, and Na are all shallow dopants, but their solubilities are much too low for doping via in-diffusion. Li is a relatively fast diffuser, Na is stable up to moderate temperatures, while P should remain immobile even at high temperatures. Na, being an interstitial dopant, is particularly suitable for ion implantation, since there is no need to displace host atoms.

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Following the advent of techniques for zero-pressure growth of diamond films there has been renewed interest in the development of diamond-based electronic devices for high-speed, high-temperature, and high-power applications. For many of these devices it is necessary to dope diamond *n* type. However, *n*-type doping of diamond has proven extremely difficult. Nitrogen, which by analogy to P in Si would be expected to be a shallow donor, is a well-known deep impurity whose properties have never been fully explained. In particular, although its EPR spectrum was measured over twenty years ago, the symmetry-breaking distortions around it were never reproduced by calculations and the reasons for their occurrence remain unexplained.

Several potential dopants were introduced into natural diamond by ion implantation,[1,2] but the only successful case to date involved Li, which was found to be an interstitial donor with an energy level at $E_c - 0.1$ eV. However, Li-doped samples become deactivated after prolonged annealing[3] although Li is still present in the sample.

In this Letter we describe the results of an extensive investigation of potential *n*-type dopants in diamond. From our *ab initio* calculations of the electronic structure of typical impurities, their solubilities, and in some cases their distortion modes and diffusion paths, there emerges a new understanding of the difficulties associated with *n*-type doping and of the properties of N in diamond. Several alternatives for *n*-type doping are examined, resulting in suggestions for the best routes to *n*-type diamond.

We have carried out calculations for N, Li, Na, and P impurities using plane-wave methods and *ab initio* pseudopotentials. Soft nonlocal pseudopotentials were constructed for C and N using the Hamann-Schlüter-Chiang procedure.[4] The C pseudopotential was previously used for studies of native defects[5] and found to reproduce well the lattice constant, the bulk modulus, and the cohesive energy of diamond when using plane waves with kinetic energies of only up to 26 Ry. For calculations involving N, we found by testing in small supercells that plane waves with energies of up to 30 Ry were needed. For Li and Na the pseudopotential matching radii had to be decreased,[6] when compared to standard values,[7] since the nearest-neighbor distance in diamond is only 1.54 Å. The impurities were placed at various positions in a large supercell. Preliminary calculations were carried out using a band-structure program, a cell size corresponding to 32 atoms in the perfect crystal, and two special *k* points in the irreducible part of the Brillouin zone. In the band-structure calculations the plane waves with energies corresponding to approximately half of the cutoff energy were included directly in the secular equation, while the remainder was treated by Löwdin perturbation theory. The final calculations utilized the Car-Parrinello method[8] and a cell corresponding to 64 atoms. The large cell size was necessary in order to obtain accurate results for the shallow impurities studied in the present paper and to investigate the distortions associated with N in diamond, which turned out to be sensitive to supercell size.

All the plane waves up to the cutoff energy were included directly in the Car-Parrinello calculations. For N, Li, and Na the positions of all the atoms in the supercell were optimized by gradient techniques using the Γ point for *k*-space sampling. As a test, the relaxation energy at the final atomic configuration for N was calculated using the Baldereschi point.[9] Because of the size of the supercell, the more accurate *k*-space sampling resulted only in minor changes (see below). Since the Keating model works well for estimating distortions around substitutional impurities, only nearest-neighbor distortions were included explicitly in the calculations for P. The relaxations of more distant shells were estimated from the Keating model.

The most common impurities and/or contaminants in natural diamond include B, N, O, and H. Boron is a well-known shallow acceptor with an energy level at 0.37 eV above the top of the valence bands,[10] while isolated N is a deep donor with a level at 1.7 eV below the top of the conduction bands.[11] The electronic levels associated with oxygen or hydrogen (if any) have not been identified.

Nitrogen is one of the few impurities in diamond for which unambiguous structural information exists. Early EPR (Ref. 12) and electron-nuclear double-resonance-technique[13] data show that substitutional N distorts in the $(\bar{1}\bar{1}\bar{1})$ direction. The latest EPR data suggest that this distortion is substantial, ~36% of the bond length.[14] The analysis of the results shows also that the unpaired electron has most of its amplitude on the nearest-neighbor carbon atom occupying the (111) position. Since N in diamond should behave like P in Si and be an effective-mass-like shallow donor, the observed distortions were very unexpected and stimulated much theoretical work.[15-20]

The pioneering extended Hückel cluster calculations by Messmer and Watkins[15] found that substitutional N introduces a triply degenerate T_2 level in the gap. Since this level is occupied by only one electron, the resulting Jahn-Teller distortion would explain the experimental data. Similar results have also been obtained in Refs. 17 and 18, which also utilized semiempirical methods. The pseudopotential calculations of Brand and Jaros[16] indicated "large" distortions, but the numerical uncertainties were too big for a more quantitative prediction. Subsequent more elaborate calculations for undistorted N, which utilized the self-consistent Green's-function method, found that the N-induced level in the gap had an A_1 symmetry.[19] Lannoo[20] has pointed out that a change in the parameters of the early calculations would lead to an A_1 level in the gap and that a pseudo-Jahn-Teller effect could be invoked to explain the experimental data. Newer modified neglect of diatomic overlap and local-density cluster calculations[21,22] have also found an A_1 level in the gap. In addition, these calculations have found that moving the N atom off center raised rather than lowered the total energy of the cluster.

In our Car-Parrinello calculations we considered both symmetric and asymmetric distortions around N. For comparison with the Green's-function calculations, we also quote results for the completely undistorted configuration. In this configuration the energy of the A_1 level is 0.7 eV below the bottom of the conduction band in our calculations, compared to 0.15 eV obtained by the Green's-function calculations of Ref. 19. Since the supercell used in the present calculations is rather large (64 atoms), the major reasons for the difference are attributed to the use in Ref. 19 of (i) Gaussian orbitals instead of plane waves, and (ii) the "scissor" operator, i.e., a rigid shift of the conduction bands with respect to the valence bands in order to match the experimental band gap of diamond.

The new results in this Letter concern the distortion modes around the N impurity. We considered the following: (i) fully symmetric relaxation of all the 64 atoms in the unit cell; (ii) movement of the N atom alone in the $(\bar{1}\bar{1}\bar{1})$ direction; (iii) movement of the N atom along $(\bar{1}\bar{1}\bar{1})$ coupled to the opposite motion of the C atom in the (111) direction; (iv) full relaxation of the atoms following (iii). The total-energy gains relative to unrelaxed N at the substitutional site are given in Table I. It is clear from the table that both the symmetric and the symmetry-breaking relaxations are important, contributing almost equal amounts to the total relaxation energy.

TABLE I. Total-energy gains for various distortion modes around substitutional N in diamond using a 64-atom unit cell. For all but the last row only the Γ point is used for k-space sampling. See text.

Unrelaxed substitutional N	0.00 eV
Full radial relaxation around N	−0.36 eV
Distortion of N and C along (111) only	−0.32 eV
Distortion of N and C and full relaxation	−0.63 eV
Distortion of N and C and full relaxation (Baldereschi point)	−0.76 eV

The origin of the symmetry-breaking relaxation can be most easily explained using valence-bond terminology.[23] The N atom prefers to be threefold coordinated, with the remaining two electrons occupying a lone-pair orbital. For molecules, when no geometry constraints are present, e.g., for ammonia, the angles between the bonds are 107.3°, constraining the lone-pair orbital to form an angle of 111.6° with the bonds. In diamond, after forming three bonds with the C atoms, the fully occupied lone pair of the substitutional N is directed towards a dangling bond of the fourth C atom. Since that dangling bond contains one electron, the Pauli principle results in an interatomic repulsion, with *both* N and the fourth C atom moving away from each other (see Fig. 1). This motion is not fully symmetric, however, with the N atom moving 11% of the bond length and the C atom moving 14%. The other nearest neighbors move only 3%. After the relaxation, the lone-pair orbital remains doubly occupied. In Fig. 2(a) we show a contour plot of its wave

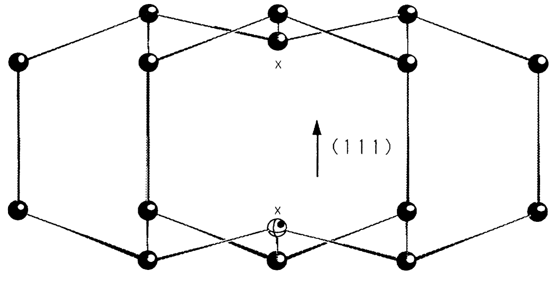

FIG. 1. The relaxation around the substitutional N in diamond. Nitrogen (the white atom) moves in the $(\bar{1}\bar{1}\bar{1})$ direction from its unrelaxed position which is marked with an ×. The C atom interacting with the N lone pair moves in the (111) direction from its unrelaxed position, also marked with an ×. The relaxation is caused by a repulsion between the N lone-pair state and a C dangling bond. The increase in the bond length is 25%. See text.

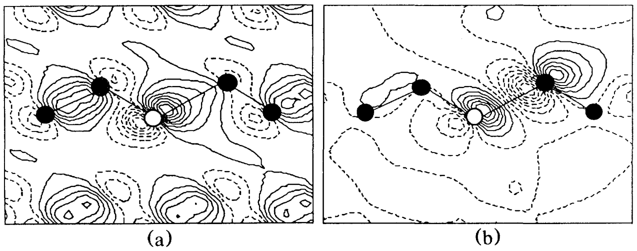

FIG. 2. Contour plots of (a) the N lone-pair orbital and (b) the N-induced EPR-active state in the gap. See text.

function at $k=0$. Because of the proximity of this orbital to the valence-band edge ($E=E_v+0.15$ eV), it contains a substantial admixture of valence-band states. The EPR-active orbital is located at $E_c-1.9$ eV. Its wave function consists of an antibonding combination of the N lone pair and C dangling bond [see Fig. 2(b)]. Most of its amplitude is on the C atom, which is in full agreement with the EPR data.

The isolated P in Si is fourfold coordinated, while the isolated N in diamond distorts and becomes threefold coordinated. The different behavior of the two impurities is due to the much greater localization of the N wave function, which is deep-impurity-like even for the undistorted N. Thus, the electronic repulsion leads to the spontaneous distortion described above. Indeed, our search using equal but opposite displacements of the N and C atoms along the (111) direction did not uncover any barrier preventing the relaxation of the N atom to its distorted ground-state configuration.

The P-H complex in Si assumes a similar distortion,[24] as does the *EL*2 center ($\mathrm{As_{Ga}}$) in GaAs.[25,26] In the P-H complex, the P atom is threefold coordinated, while the adjacent Si atom moves away in order to bond to an interstitial H atom. In the *EL*2 center, the fully symmetric substitutional site is the ground state and the distorted site is metastable and accessible only following an electronic excitation. The electrons associated with the threefold-coordinated P and $\mathrm{As_{Ga}}$ also occupy lone-pair states.

Turning to other *n*-type impurities, we have carried out calculations for P, Li, and Na. As expected, P strongly prefers the substitutional site, while Li and Na strongly prefer the interstitial site. All three impurities are shallow donors, with the approximate positions of the donor level at about 0.3 eV below the bottom of the conduction band for Na, 0.2 eV for P, and 0.1 eV for Li.[27]

In choosing a suitable donor for diamond, however, one has not only to consider its energy level but also its solubility and mode of incorporation. The equilibrium solubility of a given impurity at a particular site can be estimated in the low-concentration limit[28] as (site density)$\times\exp(-E_F/kT)$, where E_F is the formation energy of the impurity in diamond measured with respect to the segregated bulk constituents, i.e., diamond and bulk N, P, Li, and Na, respectively. The formation energies for several impurities are shown in Table II. For nitrogen it is negative, explaining the prevalence of N in natural diamond. For P, Li, and Na, however, the formation energies are positive and very large, leading to extremely small equilibrium solubilities.

TABLE II. Calculated formation energies of neutral impurities in diamond measured relative to the respective bulk reservoirs (diamond and bulk impurities; see text).

Nitrogen	−3.4 eV
Phosphorus	10.4 eV
Lithium	5.5 eV
Sodium	15.3 eV

There are several reasons for these large formation energies. The covalent radius of P is 1.13 Å, compared to 0.77 Å for C. Since the diamond lattice is very stiff, the outward relaxation of the nearest neighbors of P is small (0.15 Å), leading to a large increase in the repulsive part of the total energy. The lack of *d* orbitals in C atoms (resulting in an inability to support overcoordination) and the very large valence electron density of diamond both lead to a repulsive potential-energy surface for self-interstitials.[5] The same factors affect the formation energy of the interstitial donors, with atomic-size effects explaining the difference between the formation energies of Li and Na.

The above results have several implications for *n*-type doping of diamond. In general, one can incorporate impurities into a material in three ways: during growth, by in-diffusion, and by ion implantation. The incorporation during growth depends on both the kinetics of the growth process and the solubility of the impurity. In-diffusion depends solely on the solubility, while ion implantation is solubility independent. Because of the large formation energies of the shallow donors considered here, it is clear that their incorporation into diamond by in-diffusion will not work. Kinetic trapping during growth may be possible although it is thermodynamically very unfavorable and likely to lead to low concentrations. Very recently, the successful doping of diamond with P has been reported[29] although the dopant concentration appears to be low and the precise nature of the doping remains to be determined.

In searching for a suitable dopant one must also consider impurity diffusion because diffusion of an impurity to the surface or complexing with structural defects leads to inactivation. For substitutional dopants, such as P, it follows from previous work on self-diffusion in diamond[5] that the most likely diffusion mechanism is the vacancy mechanism. Since the formation energy of the carbon vacancy is 4.3–7.2 eV, depending on the position of the Fermi level, and its migration energy is 1.7–1.9 eV (see Ref. 5), P should be immobile even under high-temperature conditions. However, if growth and/or processing results in injection of vacancies, the activation energy becomes equal to the migration energy and deactivation may occur.

For interstitial impurities occupying tetrahedral sites the most likely diffusion path involves motion along the interstitial channel with the hexagonal interstitial site being the saddle point.[30] The activation energy for this process is given by the difference in total energies of the two sites. For Li this difference is 0.85 eV, while for Na it is 1.4 eV. The greater barrier for Na is due to its larger atomic size, which forces a significant outward relaxation at both the tetrahedral and the hexagonal sites (0.19 and 0.26 Å, respectively). Since the nearest-neighbor distance is smaller at the hexagonal site, the atomic-size effect is greater at this site and the barrier increases. Li is thus mobile at moderate temperatures and the observed deactivation of Li in ion-implanted samples after prolonged annealing[3] is most likely due to trapping of the diffusing Li at implantation-induced lattice defects.

Although diamond is very difficult to anneal, a recently developed technique[31,32] has led to a much reduced implantation damage when B was coimplanted with C. For an interstitial dopant, the coimplantation step is not needed. Since the activation barrier for the diffusion of Na is substantially larger than that of Li and the implantation damage is only weakly dependent on the mass of the ion,[2] Na should be the preferred interstitial dopant.

In summary, we have studied N, P, Li, and Na donor impurities in diamond. Nitrogen, which is a deep donor, occupies a substitutional site distorted along the (111) direction. The reason for the distortion is an antibonding interaction between the N lone-pair orbital and a C dangling bond. The donor electron has most of its amplitude on the C atom, in complete agreement with the EPR data. P, Li, and Na are shallow donors, but their solubilities are very low. Therefore, doping by in-diffusion will not work and these impurities need to be either incorporated by ion implantation or kinetically trapped during growth. Since Na is an interstitial dopant, it is particularly suitable for ion implantation. There is no need to displace host atoms and the self-implantation step, necessary for substitutional dopants, can be avoided.

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