Shallow Donor State Due to Nitrogen-Hydrogen Complex in Diamond

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(Received 26 January 2001; published 25 January 2002)

Based on an *ab initio* calculation, we propose a possible shallowing of a nitrogen (N) donor in diamond, in contrast to the traditional thinking that it is very deep. A complex defect of N and hydrogen (H), N-H-N, should be much shallower than an isolated N donor. A qualitative scenario for formation of the N-H-N defects is presented. The existence of this complex is strongly suggested by a recent discovery of a new muonium center in N-rich diamond.

DOI: 10.1103/PhysRevLett.88.066402 PACS numbers: 71.55.–i, 71.15.Mb, 71.20.–b, 81.05.Uw

Wide band gap semiconductors are superior to silicon regarding their electrical properties [1]. Diamond is a very important wide band gap semiconductor because of its large energy gap (5.5 eV). Even though diamond is of an indirect transition type, nonlinear emission of free excitons appears to occur from synthetic undoped diamond at room temperatures (RT) [2]. If the population of free carriers in diamond would be kept sufficiently large by efficient n- as well as p-type doping, then high-density free excitons could be prepared in diamond at RT to open a way toward an application of a diamond pn junction to a light source operating in the ultraviolet regime [3].

However, there is a serious problem in doping of wide band gap semiconductors. Either, not both, p- or n-type doping is much easier than the other [4]. Diamond [5] can be "efficiently" [6] doped p-type with boron (B) [7]. In sharp contrast, an efficient n-type dopant in diamond has not yet been established.

Intuitively, nitrogen (N) at a substitutional site (N_{sub} [8]) seems to be a "natural" donor in diamond, from an analogy to a substitutional phosphorus (P_{sub}) in silicon. In reality, N_{sub} in diamond creates a deep donor state in the gap, $E_{\mathrm{d}} \sim E_{\mathrm{CBM}} - 1.7$ eV [9–12]. Thus N has been traditionally recognized useless as an efficient donor in diamond. The N's are observed in several forms [13] in addition to N_{sub}: a pair of adjacent N_{sub}'s (*A* center), four N_{sub}'s surrounding a single vacancy (*B* center), and platelets, none of which have shallow donor states.

The P_{sub} is a representative candidate donor in diamond ($E_{\mathrm{d}} \sim E_{\mathrm{CBM}} - 0.5$ eV [14,15]). However, the P incorporation into diamond is much less efficient than B doping [16], and the electron mobility of P-doped diamond (~ 200 cm^2/V s [17]) is lower than the hole mobility of the B-doped counterpart (~ 2000 cm^2/V s [7]). The low solubility of P_{sub} is due to its high formation energy [10]. The high resistivity results from preferential formation of complexes of P with a vacancy (V), which are deep acceptors to compensate any donors [18].

In this paper, we challenge the above traditional thinking of N doping of diamond. Since the N content in diamond is high, typically ~ 0.1 atomic per cent (at. %) [19], one may *utilize* them rather than try to *remove* them. Formation of complexes of N with other impurities is a possible way to activate the N defects. The experimental feasibility of defect production must be seriously assessed when selecting the components of the complexes, namely, (i) the form of N defect (N_{sub}, *A* center, *B* center, or platelet) and (ii) the element as the counterpart of the N complex. We select the *A* center and hydrogen (H) as the ingredients of the complex [20]. The *A* centers are very likely to form by annealing an N-rich diamond [13] (the binding energy is ~ 4 eV per pair in our calculation). In addition, H is also abundant in diamond, 0.1 at. % [21,22], similar to N.

On the basis of *ab initio* calculations, we find that an N-H-N complex where two N_{sub}'s in the *A* center sandwich H (Fig. 1) exhibits a much shallower donor character ($E_{\mathrm{d}}^{\mathrm{GGA}} = E_{\mathrm{VBM}} + 4.42$ eV [23]) than an isolated N_{sub}

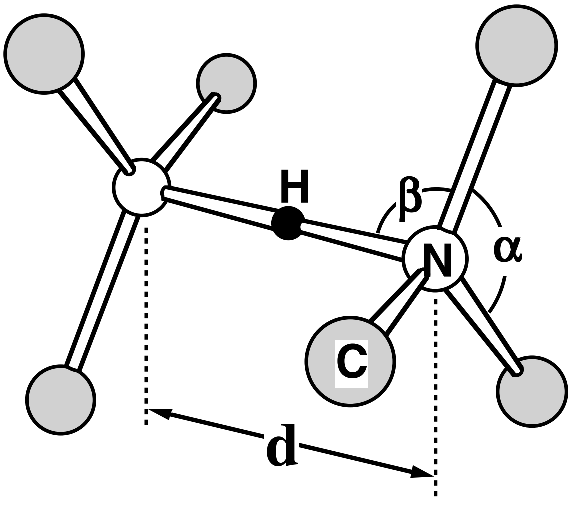

FIG. 1. Optimized structure of the N-H-N defect. Only the C atoms nearest to the N atoms are illustrated for clarity.

($E_{\mathrm{d}}^{\mathrm{GGA}} = E_{\mathrm{VBM}} + 3.36$ eV). We propose a possible scenario leading to generation of the complexes.

We adopt an *ab initio* theoretical method to study atomic and electronic structures and also energetics of N defects in diamond. The electronic structures of defects are calculated based on density-functional theory [24] within GGA [23,25] to the exchange-correlation energies. The defect structure is modeled in a simple cubic supercell with the edge being 7.162 Å long. The wave functions are expanded in plane-wave basis sets up to 25 Ry. The ultrasoft [26] pseudopotentials are used for carbon (C), N, and H. The augmentation functions are expanded in plane waves up to 400 Ry [27].

Figure 1 shows the optimized structure of the N-H-N defect in diamond. It has D_{3d} symmetry. The H sits in the middle of the two N atoms [28]. The N-N distance d and bond angles α and β (see Fig. 1 for the definitions of d, α, and β) are 2.26 Å, 117.5°, and 99.2°, respectively. For the A center, $d = 2.20$ Å, $\alpha = 117.0°$, and $\beta = 100.0°$, meaning that insertion of H between two N's does not substantially induce additional deformations of the lattice, except the elongation of the N-N distance by ~3%.

We demonstrate an aspect of the H-induced shallowing of the N donor in diamond. Based on total density of states of the N-H-N defect, its donor level is estimated to be $E_{\mathrm{d}}^{\mathrm{GGA}} = E_{\mathrm{VBM}} + 4.42$ eV [23], ~1.1 eV shallower than $E_{\mathrm{d}}^{\mathrm{GGA}}$ of $\mathrm{N_{sub}}$, $E_{\mathrm{VBM}} + 3.36$ eV. Regarding the *experimental* activation energy of $\mathrm{N_{sub}}$, $E_{\mathrm{VBM}} + 3.8$ eV, we expect that the donor level of N-H-N may be $E_{\mathrm{VBM}} + 4.9$ eV.

Another aspect of the shallowing is that the donor state of N-H-N is delocalized over the surrounding carbon atoms, although it is not effective-mass-like. As is clear from Fig. 2, the delocalization originates from the *antibonding* combination between the wave functions just at the N-H-N defect and p orbitals of six carbon atoms neighboring N, the latter stemming from the CB states of diamond.

Now we study formation energy (E_{form}) of the N-H-N defect (Fig. 3) in comparison with those of other typical defects, $\mathrm{N_{sub}}$, the A center, a single vacancy (V), and its nitrogenated ($V\mathrm{N}_x, 1 \leq x \leq 4$) as well as hydrogenated ($V\mathrm{H}_y, 1 \leq y \leq 4$) forms, H_{BC} (H at the C-C bond center) and H_2^* (H_{BC} plus another H at the antibonding site).

We calculate E_{form} with respect to N and H reservoirs adsorbed on the diamond surface [32]. This is motivated by the fact that the population of N atoms doped during chemical vapor deposition (CVD) growth of a diamond crystal significantly depends on its surface orientation [33]. In order to explain this result, we expect that N atoms are on the diamond surface for a time long enough to establish a partial equilibrium with those in the bulk crystal. Although some of the N atoms should desorb back into the vapor, the remaining atoms should be embedded in the bulk since the crystal itself is growing. Here we consider the (100)-(2 × 1) diamond surface. We estimate the maximum values of N and H chemical potentials from the total energies of N-dimer-row C(100)-(2 × 1):N [Fig. 3(b)] and monohydride C(100)-(2 × 1):H [Fig. 3(c)] structures, which correspond to an N-rich and H-rich phases, respectively (see also the caption of Fig. 3). The chemical potential of the N-H "mixture" on the C(100) surface is assumed to be the total energy of the structure shown in Fig. 3(d) [34].

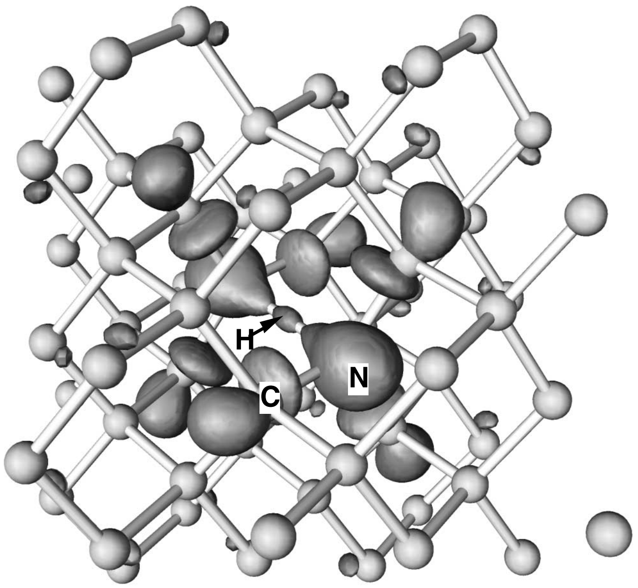

FIG. 2. Squared amplitude of the HOMO state of the N-H-N complex. The graphics is produced with MACMOLPLT [29].

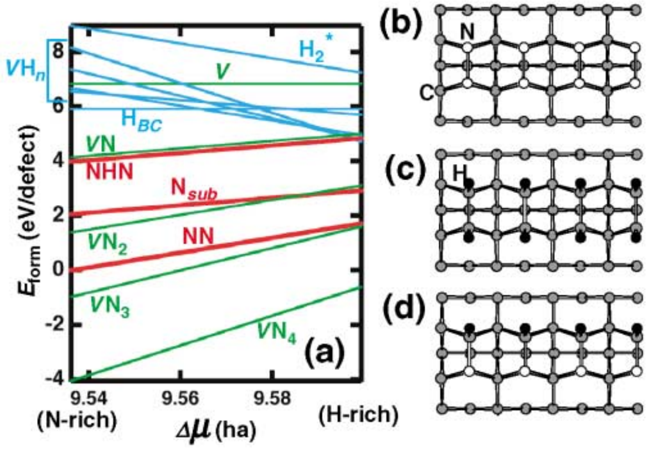

FIG. 3 (color). (a) Calculated formation energies (E_{form}) of various N- and H-related defects in diamond, as a function of $\Delta\mu = \mu_{\mathrm{H}} - \mu_{\mathrm{N}}$, where μ_{H} and μ_{N} are chemical potentials of H and N, respectively. E_{form} is defined for a window of $\Delta\mu$, which is determined from $\mu_{\mathrm{N}} \leq \mu_{\mathrm{N}}^{\max}$, $\mu_{\mathrm{H}} \leq \mu_{\mathrm{H}}^{\max}$, and $\mu_{\mathrm{N}} + \mu_{\mathrm{H}} = \mu_{\mathrm{N+H}}$. $\mu_{\mathrm{N}}^{\max}$, $\mu_{\mathrm{H}}^{\max}$, and $\mu_{\mathrm{N+H}}$ are derived from the total energies of adsorbed impurities shown in panels (b), (c), and (d), respectively [30]. The chemical potentials are calculated at $T = 0$ [31].

As is clear in Fig. 3(a), E_{form} of N-H-N is lower than those of V as well as of other H-related defects. At the same time, it is higher than those of VN_x as well as of N_{sub} and the A center. Since V's may exist in CVD-grown diamond at a high content [35], it is highly expected to have a substantial population of the N-H-N defects. However, the populations of the B centers (VN_4) and possibly of the VN_3 defects may become extremely large because of their negative formation energies. Thus, there are two conditions for successful generation of N-H-N defects in diamond: (i) *Minimize* the number of V's but (ii) *maximize* the content of N. The CVD growth of diamond with a low growth rate satisfies (i), by suppressing the C/H ratio in the gas source. One must yet maintain the N-doping rate and the diamond growth speed high enough to let as many of the N atoms on the surface as possible be incorporated in the crystal prior to their desorption, in order to meet (ii). Therefore there should be an optimum growth and N-doping rates to compromise (i) and (ii).

Once the N atoms could be doped in diamond with a low concentration of V's, the A centers (N-N) and H_{BC}'s would be the dominant N and H defects to lower the total formation energy of the impurities. A subsequent annealing of the sample may induce the diffusion of H atoms and their trapping at N-N with an exothermic reaction: N-N + H_{BC} → N-H-N + 2 eV.

Thorough tests for previously proposed defects using $2N_{sub} + Al_{sub}$ [36] and $2N_{sub} + B_{sub}$ [37] complexes reveal that both are actually much deeper than our N-H-N defect. We find, for N-Al-N, $E_d^{GGA} = E_{VBM} +$ 3.73 eV, only slightly shallower than N_{sub} ($E_d^{GGA} = E_{VBM} + 3.36$ eV), in contradiction to the report by Yu *et al.* [36,38]. Our structure of N-Al-N is similar to N_{sub}, which is the cause of the deep donor level. An N-N-B defect is the most favorable among the candidates of (2N + B) complexes, with the total energy being 0.7 eV lower than that of N-B-N (C_{2v}) proposed by Yoshida *et al.* [37]. The defect HOMO [23] state of N-N-B is so deep ($E_d^{GGA} = E_{VBM} + 1.43$ eV) that it is a *deep acceptor*. The structure of N-N-B resembles that of the A center, explaining why its HOMO level is extremely deep. Thus n-type codoping ideas using 2N + B and 2N + Al are both unlikely to work.

A new muonium center (Mu_X) has been discovered by Machi *et al.* in N-rich diamond [39]. They propose that Mu_X is a muonium sitting between two N atoms in an A center [28]. Their result suggests a possibility of the N-H-N defects having a real existence in N-rich diamond. Since H is much heavier than a muonium, H should be trapped in the middle of the A center for a much longer time than the muonium.

Finally, the *absolute depth* of the N-H-N donor level ($E_{CBM} - E_d$) is still illusive due to the GGA band-gap-error problem (our GGA band gap of diamond is 4.27 eV). Thus, further theoretical studies will have to be made for its unambiguous determination using higher-level methods such as the *GW* approximation [40]. Detailed experimental investigations will also be necessary to detect any fingerprint of existence of N-H-N complexes in diamond.

In conclusion, we propose a possible shallowing of an N donor in diamond, in opposition to the traditional thinking that it is a very deep donor. Forming an N-H-N complex may make an N donor in diamond much shallower ($E_d^{GGA} = E_{VBM} + 4.42$ eV) than an isolated N_{sub} ($E_d^{GGA} = E_{VBM} + 3.36$ eV).

T. M. thanks Professor Jacques Chevallier for motivating him to this study. This work is partly supported by NEDO and TACC.

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[6] When a dopant has a high solubility and produces carriers with a low activation energy in a host crystal and the doped crystal exhibits good electrical transport properties such as a high carrier mobility, it may be called an "efficient" dopant.
[7] S. Yamanaka *et al.,* Jpn. J. Appl. Phys. **37**, L1129 (1998).
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[9] "E_d," "E_{CBM}," and "E_{VBM}" stand for the energy positions of a donor level, the conduction-band minimum (CBM), and the valence-band maximum (VBM), respectively.
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[23] We estimate an approximate value of E_d as the difference of the highest-occupied molecular-orbital (HOMO) level of the optimized defect from the VBM of a defect-free diamond, by adjusting the positions of the major peaks of the valence bands of the defect to those of the bulk diamond. The artificial dispersion of the donor state due to finiteness of the supercell is roughly 0.5–1 eV, which does not affect seriously the determination of the donor level position. We quote $E_\mathrm{d}^\mathrm{GGA}$ [E_d as calculated with generalized gradient approximation (GGA)] relative to VBM. We do not rely on any *ad hoc* correction such as that proposed by Baraff and Schlüter [G. A. Baraff and M. Schlüter, Phys. Rev. B **30**, 1853 (1984)] but present the "original" GGA donor level $E_\mathrm{d}^\mathrm{GGA}$.

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[27] The self-consistent field iterations are continued until the total energy converges to $\sim 3 \times 10^{-6}$ eV/atom. The atomic positions of all atoms in supercell are relaxed until the residual forces are less than ~ 0.06 eV/Å. The integration over the first Brillouin zone (BZ) is performed on a $4 \times 4 \times 4$ regular mesh. With these parameters, the total-energy difference converges with the numerical uncertainty no greater than ~ 0.01 eV per defect.

[28] Symmetry-unrestricted optimizations of the N-H-N structure show that it is stable against the off-axis distortions. Machi *et al.* [39] find that Mu_X (see text for definition of Mu_X) occupies a site of less than axial symmetry, suggesting that the N-Mu-N bond is bent. This bond bending may happen as a result of quantum motions of a muonium or of any stress due to other defects than Mu_X in real diamond crystals, which we do not consider in the present study.

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[31] Temperature dependence of the impurity chemical potentials is small. For example, μ_H at $T = 1000$ K is ~ 0.4 eV per H higher than that at $T = 0$ K, by using the surface phonon modes calculated at $\Gamma_{2\times 1}$ of the surface BZ of monohydride C(100)-(2×1):H [B. Sandfort, A. Mazur, and J. Pollmann, Phys. Rev. B **54**, 8605 (1996)].

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