Phosphorus and sulphur doping of diamond

L. G. Wang and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401
(Received 9 May 2002; published 16 October 2002)

Previous calculations on *n*-type doping of diamond by P and S predicted that S has a shallower level and a higher solubility than P. Our first-principles calculations show that the opposite is true: Phosphorus impurity in diamond gives rise to a shallower donor level, and has a higher bulk solid solubility than sulphur. This agrees with the trends expected from the strength of the atomic pseudopotentials. We predict that coherent epitaxial expansion would substantially increase the solubility of P, and that complex formation of P with H is exothermic, also leading to passivation of the P donor action; removal of H then is needed to achieve good *n*-type characteristicy.

Diamond can be *p*-type doped by boron acceptors,[1] but its *n*-type doping, via donors such as phosphorus or sulphur, is very difficult.[2–5] In general, three factors tend to limit doping: (i) Insufficient solubility: the impurity solubility $N_I = N_0 e^{-\Delta H_f/kT}$, is controlled by the formation enthalpy $\Delta H_f^{(q)}(\mu, \epsilon_F)$ of the dopant of charge q at the Fermi energy ϵ_F and chemical potential μ. Large positive $\Delta H_f^{(q)}(\mu, \epsilon_F)$ implies limited solubility. (ii) Energetically too deep level: i.e., the energy $\epsilon(q/q')$ of the impurity electrical transition level is too distant from the host-crystal valence-band maximum [for $(0/-)$ acceptors], or from the conduction-band minimum [for $(0/+)$ donors]. (iii) Charge compensation: i.e., the ability of the host crystal to spontaneously create intrinsic defects that compensate the intentionally introduced carriers.

Factors (i) and (ii) can sometimes be circumvented by the choice of different dopant impurities, or by changing growth conditions which can alter ΔH_f: a large bulk ΔH_f may be reduced either via coherent epitaxial growth[6] or surface reconstruction.[7] Indeed, "epitaxy-enhanced solubility" corresponds to the reduction of ΔH_f via an epitaxial destabilization of the strained constituents on the growing surface,[6] whereas "surface enhanced solubility" corresponds to the reduction of ΔH_f via the bonding constrained imposed by surface dimers.[7] In contrast to factors (i) and (ii) that may sometimes be engineered deliberately, factor (iii) is the ultimate factor limiting dopability, as it reflects the response of the host crystal itself to the sheer existence of free-carriers.

For most III-V semiconductors one can identify soluble and shallow-level dopants, so the ultimate bottleneck for achieving a high carrier density in these semiconductors is factor (iii), i.e., the spontaneous formation of electron-compensating cation vacancies or *DX* centers.[8] In contrast, it appears that the *n*-type dopability of diamond is still limited by factors (i) and (ii), namely, the solubility and ionizability of the donors used to date. For example, dopants, which sizewise can fit into the tight diamond lattice, have deep levels. This is the case of N,[9] O,[9,10] and Cl,[10] whereas F is an acceptor in diamond.[11] Li and Na have been predicted[12] to be shallow donors in diamond when occupying interstitial sites; however, experiments[3] failed to obtain *n*-type diamond by doping Li and Na. It appears that P and S are the most prom-

ising *n*-type dopants in diamond.[4,5,13] Koizumi *et al.*[4] unambiguously observed *n*-type features of P-doped diamond during, chemical vapor deposition (CVD) homoepitaxial growth. For S, experimental results are controversial. S-doped diamond was shown in Ref. 5 to be *n*-type; however, later reexamination by Kalish *et al.*[14] showed these samples to be *p*-type. Nishitani-Gamo *et al.*[13] also observed *n*-type properties of S-doped homoepitaxial (001) diamond, whereas Garrido *et al.*[15] could not observe a donor state for S-doped CVD diamond, except for an acceptor state at 479 meV above the valence-band maximum (VBM) which may be related to complex formation due to the presence of S. On the theoretical side, first-principles calculations of formation enthalpies and donor levels for P and S in diamond have produced conflicting results: whereas some authors[9,16,17] showed that sulphur has a shallow donor level, other authors[18,19] predicted a deep level. Theoretical results do not agree with each other on whether P or S has a higher bulk solubility as well.[9,18] These conflicting results (both theoretical and experimental) raise a question about what are the basic chemical trends at play for dopants in semiconductors, such as P and S in diamond.

In the present paper, we have carefully recalculated the formation energies and transition energies of isolated P and S (as well as B, for comparison) in diamond using the first-principles supercell method. We find that P is both shallower and more bulk soluble than S in diamond. We show that this is consistent with P having a weaker pseudopotential than S, and with the fact that its wave function is more extended. We find that previous calculations either used inconsistent expressions for ΔH_f and $\epsilon(q/q')$, or were insufficiently converged (e.g., used an incompletely relaxed atomic geometry, or only a single *k* point). Our calculated bulk formation energy of P is still very high (6.65 eV), implying a very low equilibrium solubility of P in bulk diamond. We then explore the possibility of epitaxially enhanced solubility,[6] finding that the formation enthalpy of P in a biaxially expanded diamond film (tensile strain) becomes lower, and the donor level becomes shallower relative to the bulk case. Thus epitaxial pseudomorphic diamond films would enhance the solubility of P. In order to clarify why it has proven difficult to obtain *n*-type conductivity in P-doped diamond, we investigate the effects of inadvertent impurities, i.e., H and its P-H complex

in diamond. As in Ref. 20, we find that H passivates both *n*- and *p*-type conductivities, i.e., H eliminates free electrons when the material is *n*-type and free holes when the material is *p*-type, and has a very deep donor level ($E_c - 3.29$ eV). Interestingly, our results indicate that the P-H complex is very stable (i.e., has a large binding energy) with respect to dissociation into isolated impurities. We thus propose that to obtain *n*-type diamond via heavy doping by P one needs to eliminate the impurity H which attaches itself to P and passivates the donor action.

We calculate the formation energy for a reaction in which P or S, with chemical potential μ, replaces a carbon atom (which then joins the surface of the sample), creating an impurity center with charge q, in equilibrium with the electron reservoir of energy ϵ_F and the chemical reservoir with potential μ. The dopant chemical potential has to meet $\mu \leq \mu$(solid), or else the dopant will precipitate as a pure solid phase. Here μ(solid) is the total energy of a solid made of the elemental dopant, e.g., orthorhombic P or S. The formation enthalpy is given by

$$\Delta H_f^{(\alpha,q)}(\mu, \epsilon_F) = \Delta H_f^{(\alpha,0)}(\mu) - q\epsilon(0/q) + q\epsilon_F. \quad (1)$$

Here $\Delta H_f^{(\alpha,0)}(\mu)$ is the formation enthalpy of the neutral ($q=0$) defect and $\epsilon(0/q)$ is the transition energy level in the gap. Both quantities are calculated from the total energy, not just from band eigenvalues. The formation energy of a neutral defect,

$$\Delta H^{(\alpha,0)} = [E_{tot}^{(\alpha,0)} - E_{tot}^{pure}] - \sum_i N_i\mu_i, \quad (2)$$

is calculated from the difference in total energy of a supercell containing defect α and a supercell of the pure host material, corrected by the chemical potential term due to the transfer of atoms from the defect supercell to the chemical reservoir. The "defect transition level $\epsilon(0/q)$" denotes the value of the Fermi energy where the defect changes from being charge neutral to having a charge q. We believe that it is the transition energy, rather than the eigenvalue, that should be compared with the experimental activation energy of the carrier. It is calculated as

$$\epsilon(0/q) = -\frac{1}{q}[E_{tot}^{(\alpha,q)} - E_{tot}^{(\alpha,0)} + qE_{VBM}], \quad (3)$$

using the difference in total energy of a supercell containing the defect α in charge state q, and the supercell with the neutral defect, corrected for charge neutrality by the term qE_{VBM}, where E_{VBM} is the zero of the Fermi level at the valence band maximum.

The total energies E_{tot} are calculated by pseudopotential plane-wave method.[21] We employ the generalized gradient approximation for the exchange-correlation potential.[22] The Vanderbilt ultrasoft pseudopotentials[23] are used to represent the interaction of the core and valence electrons for these atoms. A $4 \times 4 \times 4$ Monkhorst-Pack grid[24] of wave vectors in the Brillouin zone of a 64-atom supercell and the plane-wave basis cutoff energy of 25.7 Ry are used in our calculations. Both host and dopant atoms in the supercell are allowed to
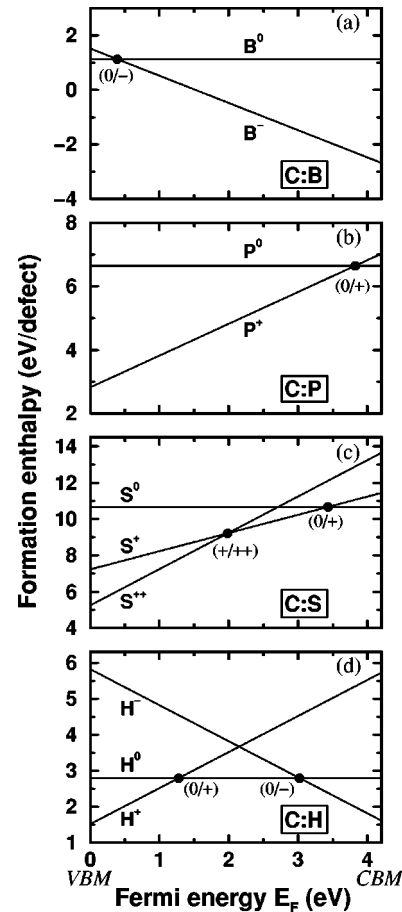

FIG. 1. Formation energies of substitutional P, S, B, and interstitial H in diamond bulk as a function of the Fermi energy. For P, S, or B we take $\mu = \mu$(solid), i.e., in equilibrium with the elemental solid. For H it is in equilibrium with free H atom. Solid dots denote transition energy levels.

relax until the force on atoms are smaller than 0.05 eV/Å. Charge neutrality is affected in the calculation by placing the balance of charge in a uniform jellium background. We correct the total energy for the leading error of the Makov-Payne scheme[25] in a charged system due to the use of a limited supercell size and periodic boundary conditions. With these parameters, the total-energy difference converges to ~ 0.01 eV per defect. For diamond we obtain a lattice constant of 3.57 Å and a bulk modulus of 4.26 Mbar, compared with experimental values of 3.57 Å and 4.42 Mbar. The calculated indirect band gap of 4.2 eV is underestimated relative to experiment (5.5 eV). After we converge the results to self-consistency for the pure host supercell with the $4 \times 4 \times 4$ grid of k points, E_{VBM} is evaluated at the Γ point. In the present work, we do not attempt to correct the band gap because the depth of donor and acceptor levels stays nearly same before and after the correction.[26]

Figures 1(a)–1(c) shows our calculated $\Delta H_f(\epsilon_F, \mu)$ as a function of ϵ_F at $\mu = \mu$(solid) for B, P and S in diamond. The crossing points for charge state q and q' provides the transition energies $\epsilon(q/q')$ denoted in Fig. 1 by solid dots. Table I summarizes the values. We see that:

(i) *Atomic configurations*: Assuming T_d symmetry at first,

TABLE I. Calculated formation energies (eV/defect) and defect transition levels (eV) of B, P, and S in diamond.

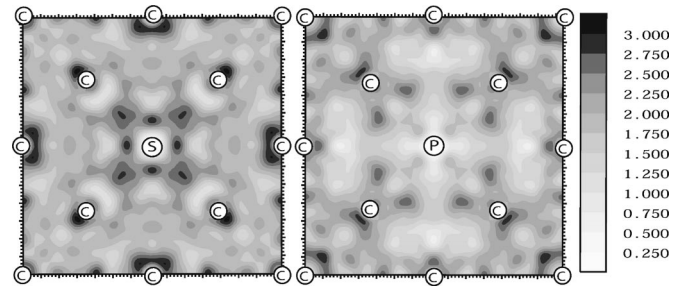|	B	P	S
$(0/+)$	-	$E_c - 0.37$	$E_c - 0.77$
$(+/++)$	-	-	$E_c - 2.22$
$(0/-)$	$E_v + 0.39$	-	-
ΔH_f	1.13	6.65	10.67

FIG. 2. Plot of the wave-function square for the dopant-induced gap state of phosphorus and sulphur in diamond projected on the (001) diamond plane.

the neutral S^0 will have an electronic configuration of t_2^2 (i.e., the threefold-degenerate t_2 orbitals are occupied by two electrons). This could lead to symmetry lowering because of the Jahn-Teller distortion. By using initially random atomic displacements and letting the system evolve away from T_d symmetry we indeed find that C_{3v} symmetry has lower energy by 0.22 eV, with a longer C-S bond at 1.96 Å and the three shorter C-S bonds at 1.68 Å. For P^0 and S^+, the atomic configuration can also have C_{3v} symmetry since the t_2 orbitals are occupied by one electron. However, we find that the atomic configuration has T_d symmetry. For P^+ and S^{2+}, we find that the atomic configuration has a T_d symmetry, as expected from the zero occupation of the t_2 orbitals. The four C-P bonds have lengths of 1.70 and 1.69 Å for P^0 and P^+, respectively. In both S^+ and S^{2+} cases the C-S bonds have the same length of 1.70 Å.

(ii) *Comparison of levels with experiment and other calculations*: Our calculated acceptor level of boron $\epsilon(0/-) = E_v + 0.39$ eV is in excellent agreement with the experimental value[27] ($E_v + 0.37$ eV). The calculated donor level of phosphorus $\epsilon(0/+) = E_c - 0.37$ eV is close to the lower limit of the experimental value which is between $E_c - 0.4$ and $E_c - 0.6$ eV.[4] Our calculated result is in good agreement with the value $E_c - 0.4$ eV of Saada et al.,[9] but deeper than the value $E_c - 0.2$ eV predicted by Kajihara et al.[12] and Gheeraert et al.[17] The difference between our result and the value predicted by Kajihara et al.[12] and by Gheeraert et al.[17] may be attributed to the incomplete lattice relaxation of atomic positions in their calculations. Indeed, our unrelaxed calculation gives a donor level $E_c - 0.26$ eV for P which is in better agreement with the results by Kajihara et al.[12] and Gheeraert et al.[17]

(iii) *Chemical trends*: The calculated P donor level ($E_c - 0.37$ eV) is shallower than the S donor level ($E_c - 0.77$ eV). The donor level we obtain for S is deeper than those obtained by Saada et al.[9] and by Zhou et al.,[16] but is shallower than those by Katayama-Yoshida et al.[19] and by Miyazaki et al.[18] This reflects the fact that the P ionic pseudopotential is weaker than that of S (see Fig. 3 in Ref. 28). In Fig. 2, we plot the wave-function square for the state in the gap induced by dopant P or S. We see clearly that the S-induced gap state is more localized than the one induced by P. Therefore, our theoretical prediction that P has a shallower donor level than S is consistent with the weaker ionic pseudopotential of P and the more extended wave function of the P-induced gap state.

(iv) *Defect formation energies*: P has a lower formation enthalpy than S, in agreement with the findings of Miyazaki

et al.[18] Our result $\Delta H_f = 6.65$ eV for neutral P is lower than the value 10.4 eV obtained by Kajihara et al.[12] This may also be attributed to an incomplete relaxation of atomic positions in their calculation. If we do not relax the atomic position in our calculation, we obtain a formation enthalpy of 9.24 eV, which is closer to the value 10.4 eV of Kajihara et al.[12] [The remaining difference may be due to technical differences, such as k-points (in their calculations only a Γ k point is used, whereas we employ a much finer k vector mesh) and type of potentials.] The formation enthalpies for both neutral P and S are in good agreement with the results obtained by Miyazaki et al.[18]

(v) *Tensile epitaxial strain can enhance the P solubility*: We have recalculated ΔH_f and $\epsilon(0/q)$ by assuming that diamond is coherently matched in the in-plane (001) direction to a substrate with larger lattice constant (a_s) than diamond (a_0). The strain in the perpendicular direction was relaxed. Our results indicate that the formation enthalpy of P is reduced from the bulk value of 6.65 eV to 4.74 and 2.89 eV for biaxially strained diamond films with the tensile strains ($a_s - a_0)/a_0$ of 4% and 8%, respectively. Thus, using tensile epitaxial diamond films may achieve a very high solubility of P. A very recent paper also indicated a large enhancement of boron solubility in silicon due to biaxial stress.[29] Under tensile epitaxial strain, both the in-plane C-C and C-P bond distances increase, leading to a lowering of the energy of the host (antibonding) conduction band maximum (CBM) and the donor level. However, the host diamond CBM is lowered more than the donor level, leading to a slightly shallower donor level in the epitaxial system.

(vi) *Hydrogen passivates phosphorus doping in diamond*: Both natural diamonds and those grown by chemical vapor deposition contain hydrogen. We investigate the effect of H on the carrier density in diamond. In agreement with Ref. 20 we find that the bond-centered site is the most stable site for isolated H with charges $q = 0$ and -1, and a site close to the bond-center for $q = +$. Figure 1(d) shows the dependence of the formation energy of H with $q = -1$, 0, and $+1$ on the Fermi energy in equilibrium with free H atom. When the Fermi energy is in the upper part of the gap, the acceptor H^- is stable, which means hydrogen is an electron killer in n-type diamond. Similarly, when ϵ_F is in the lower part of the gap, the donor H^+ is stable, which means hydrogen is a hole killer in p-type diamond. When the Fermi level is

around midgap, H^0 is stable.[30] If we dope diamond with P, hydrogen tends to combine with P at the antibonding site (see Ref. 19) forming P-H complexes. The calculated binding energies of the neutral P-H complex in diamond are 2.45 eV with respect to neutral H and P, and 1.85 eV with respect to P^+ and H^-. Our binding energy results are reasonable agreement with other theoretical values of 2.56 eV (Ref. 19) and 3.1 eV (Ref. 20) for dissociation into neutral components, and are larger than the value of 1.0 eV (Ref. 20) for dissociation into charged components. The calculated (0/+) transition energy of the P-H complex is $E_c - 3.29$ eV, which is very deep and does not contribute to conductivity. Our result is consistent with $E_c - 3.0$ eV in Ref. 20. Previous work[20,31] also indicated that H combining with B (B-H complexes) results in B losing effect as an acceptor. This explains why n-type conductivity cannot be obtained for H-containing diamond samples doped with phosphorus. Because of a relatively low bulk solubility of P controlling the H concentration in P-doped diamond is even more crucial in order to obtain n-type conductivity.

In conclusion, we have investigated by first-principles calculations P and S as donors in diamond. Our results indicate that P is more soluble in bulk diamond and has a shallower donor level, which is consistent with a weaker strength of P ionic pseudopotential. We suggested a biaxially expanded epitaxial diamond film can enhance the solubility of P and may result in a good n-type conductivity. However, we show that controlling H concentration in P-doped diamond is crucial in obtaining n-type conductivity because H tends to compensate and passivate P as a donor.

[1] S. Yamanaka *et al.*, Jpn. J. Appl. Phys. **37**, L1129 (1998).

[2] R. Kalish, Diamond Relat. Mater. **10**, 1749 (2001).

[3] G. Popovici and M.A. Prelas, Diamond Relat. Mater. **4**, 1305 (1995).

[4] S. Koizumi *et al.*, Appl. Phys. Lett. **71**, 1065 (1997); Diamond Relat. Mater. **7**, 540 (1998).

[5] I. Sakaguchi *et al.*, Phys. Rev. B **60**, R2139 (1999).

[6] D.M. Wood and A. Zunger, Phys. Rev. Lett. **61**, 1501 (1988); Phys. Rev. B **40**, 4062 (1989); A. Zunger and D.M. Wood, J. Cryst. Growth **98**, 1 (1989).

[7] S.B. Zhang and A. Zunger, Appl. Phys. Lett. **71**, 677 (1997).

[8] S.B. Zhang, S.H. Wei, and A. Zunger, Phys. Rev. Lett. **84**, 1232 (2000).

[9] D. Saada, J. Adler, and R. Kalish, Appl. Phys. Lett. **77**, 878 (2000).

[10] S. Pöykkö, M. Kaukonen, M.J. Puska, and R.M. Nieminen, Comput. Mater. Sci. **10**, 351 (1998).

[11] G. Popovici *et al.*, J. Appl. Phys. **77**, 5625 (1995).

[12] S.A. Kajihara, A. Antonelli, J. Bernholc, and R. Car, Phys. Rev. Lett. **66**, 2010 (1991).

[13] M. Nishitani-Gamo *et al.*, Diamond Relat. Mater. **9**, 941 (2000).

[14] R. Kalish, A. Reznik, C. Uzan-Saguy, and C. Cytermann, Appl. Phys. Lett. **76**, 757 (2000).

[15] J.A. Garrido *et al.*, Phys. Rev. B **65**, 165409 (2002).

[16] H. Zhou *et al.*, J. Appl. Phys. **40**, 2830 (2001).

[17] E. Gheeraert, S. Koizumi, T. Teraji, and H. Kanda, Solid State Commun. **113**, 577 (2000).

[18] T. Miyazaki and H. Okushi, Diamond Relat. Mater. **10**, 449 (2001).

[19] H. Katayama-Yoshida, T. Nishimatsu, T. Yamamoto, and N. Orita, J. Phys.: Condens. Matter **13**, 8901 (2001); T. Nishimatsu, H. Katayama-Yoshida, and N. Orita, Physica B **302-303**, 149 (2001).

[20] J.P. Goss *et al.*, Phys. Rev. B **65**, 115207 (2002).

[21] J. Ihm, A. Zunger, and M.L. Cohen, J. Phys. C **12**, 4409 (1979); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[22] J. P. Perdew, in *Electronic Structure of Solids '91,* edited by P. Ziesche and H. Eschring (Akademie-Verlag, Berlin, 1991); J.P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).

[23] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[24] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

[25] G. Makov and M.C. Payne, Phys. Rev. B **51**, 4014 (1995).

[26] C. Kilic and A. Zunger (unpublished).

[27] A.T. Collins and A.W.S. Williams, J. Phys. C **4**, 1789 (1971).

[28] A. Zunger, in *Structure and Bonding in Crystals*, edited by M. O'Keefe and A. Navrotsky (Academic Press, New York, 1981), Vol. I, p. 73.

[29] B. Sadigh *et al.*, Appl. Phys. Lett. **80**, 4738 (2002).

[30] The "effective U" of the system $U = \epsilon(0/-) - \epsilon(0/+)$ is 1.74 eV. This large positive U for H in diamond is because H is stable at the bond center (or one close to it) for all charge states ($q = -1, 0, +1$). Our value of U is larger than that in Ref. 20 because we consider the total energy correction in a charged supercell calculation.

[31] S.J. Breuer and P.R. Briddon, Phys. Rev. B **49**, 10 332 (1994); S.P. Mehandru and A.B. Anderson, J. Mater. Res. **9**, 383 (1994).