Phosphorus and sulphur doping of diamond

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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" responds 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

!. 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

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 $\epsilon(0/-)$ $= E_v +$

around midgap, H^0 is stable.[30]