

Electronic States of Dopants in Diamond Calculated by a DV-X α Method

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Electronic state of dopants in diamonds were calculated by a DV-X α method and the stability of the impurity was discussed on the basis of bondorder B_o . A cluster model applied was [AC₂₈H₃₆] (A=B P, or N) with T_d or C_{3v} symmetry. As for an N-doped cluster, N-C bonds were stabilized by the introduction of structural relaxation from T_d to C_{3v} symmetry. On the other hand, calculated B_o for B-C bond was independent of structural relaxation from T_d to C_{3v} symmetry. Consideration of Jahn-Teller effect was suggested to be important to discuss the boron doped diamond.

1. Introduction

Diamond is a candidate material for electronics devices because of its high hole mobility, thermal conductivity and wide band gap[1]. However, electron doping into diamond has not performed yet, though hole doping could be obtained by boron substitution[2]. It is considered that localization of doped electrons takes place due to lattice relaxation around doped impurities and/or segregation of impurities. For example, EPR measurements suggested that a doped nitrogen has not T_d but C_{3v} symmetry and the nitrogen atoms tend to form a cluster of N_x in diamond[3].

Molecular orbital (MO) calculation has been applied to elucidate the electronic and structural properties of diamond[4]. The formation of N_x cluster has been discussed on the basis of the MO calculation[5]. In our previous work[6], the electronic state of Ni-ion in diamond was calculated by a DV-X α method, and electron paramagnetic resonance spectra were assigned. Then, it was indicated that the DV-X α method is applicable for the calculation of impurities in diamond.

In the present study, the DV-X α method was applied to discuss chemical bonding states of impurities in diamonds, i.e. nitrogen N, phosphorus P and boron B.

2. Calculation Method

A cluster $[C_{29}H_{36}]$ of T_d symmetry, indicated in Fig. 1, was applied for the calculation of pure diamond. As for the impurity-doped diamond, a central carbon atom in the $[C_{29}H_{36}]$ cluster was substituted by nitrogen, boron or phosphorus, i.e. $[AC_{28}H_{36}]$ (A= N, B or P). Dangling bonds on the cluster surface were terminated by hydrogen atoms as shown in Fig.1.

Lattice relaxation effect was taken into account by reducing the symmetry of cluster

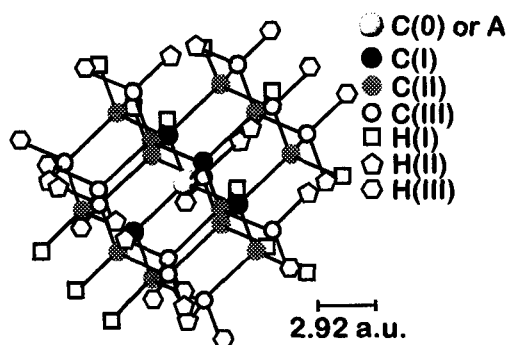


Figure 1 A cluster model $[C_{29}H_{36}]$. A carbon atom, indicated by C(0) was substituted by nitrogen, boron or phosphorus atom.

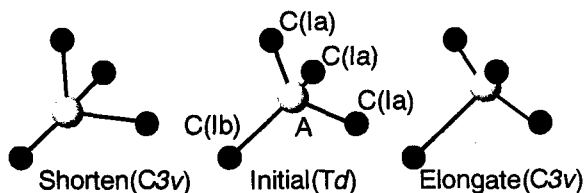


Figure 2 Assumed lattice relaxation from T_d to C_{3v} symmetry.

from T_d to C_{3v} in the manner shown in Fig.2:

A atom was displaced from its initial position to the position where A-C(Ib) bond length elongates or shortens. The displacement of C(1), C(II) and C(III) atoms was disregarded in the present study.

Effective charge of each atom in a cluster was evaluated by a Mulliken population analysis. Stability of doped atoms was estimated from bondorder between a substituted A atom and an adjacent carbon atom, C(1): the bondorder is defined as the summation of overlap population for a chemical bond.

3. Results and Discussion

3.1 Nitrogen substitution

The molecular orbital calculation for a $[NC_{28}H_{36}]$ cluster gave different results for C_{3v} and T_d symmetries though atom positions were fixed. This result suggests that structural relaxation should be incorporated into the electronic state calculation for the nitrogen center in diamond [5].

Figure 3 indicates a relation between lattice relaxation and bondorder B_o of N-C bonds in the $[NC_{28}H_{36}]$ cluster. B_o for N-C bonds was less than that for C-C bonds, i.e. 3.0. As indicated in Fig.3, B_o for N-C(Ia) bonds was much larger than that for N-C(Ib) bond. This result suggests that a nitrogen atom makes chemical bonds with only three carbon atoms C(Ia) like an NH_3 molecule and has little interaction with another carbon atom C(Ib). The value of B_o was saturated with the increase of N-C(Ib) distance and constant over

106% elongation. The saturation is due to simultaneous increase of bonding and antibonding component of N-C(Ia) bonds caused by shorten N-C(Ia) distance. The elongation of N-C(Ib) distance in diamond was estimated from EPR observation, i.e. 120--128%[3]. However, converged result was not obtained for the cluster of over 110% elongation. It is indicated that the displacement of C(Ia) and/or C(Ib) atom must

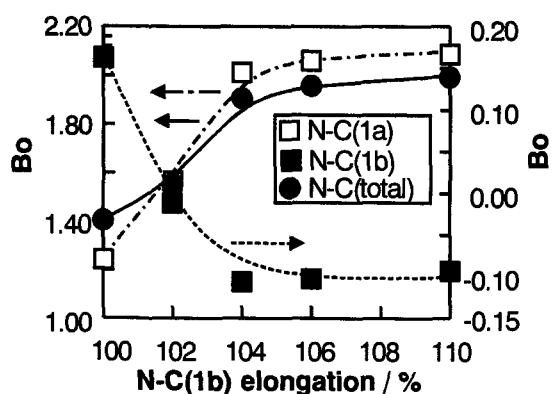


Figure 3 Relation between bond order and lattice relaxation for $[NC_{28}H_{36}]$.

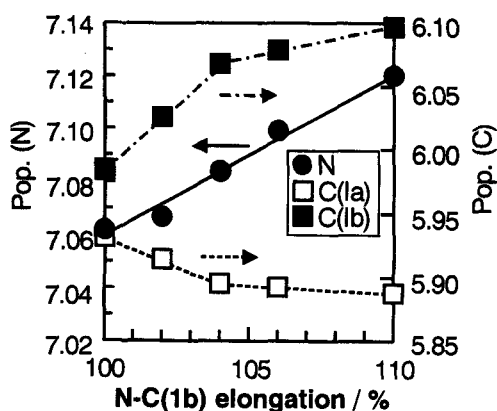


Figure 4 Relation between lattice relaxation and electron population of atoms in $[NC_{28}H_{36}]$ cluster in C_{3v} symmetry.

be taken into account to estimate the most arrangement of nitrogen center.

Effective charge of each atom also depended on the N-C(Ib) distance, as indicated in Fig.4. Electron transfer from C(Ia) to C(Ib) and N increased with the N-C(Ib) distance. The electron doped with nitrogen mainly localized at C(Ib) site: 60% of lone-pair electron was ascribed the C(Ib) site at the elongation of 110%. This result indicated that the doped electron localized between the N-C(Ib) bond resulting in the elongation and stabilization of the N-C(Ib) bond.

3.2 Boron Substitution

As for a cluster $[BC_{28}H_{36}]$, MO calculation converged for T_d symmetry but not for C_{3v} symmetry in which atom positions were the same as the T_d symmetry. This is due to the splitting of an impurity level by symmetry lowering. The hole introduced by boron doping occupied a molecular orbital t_2 in the T_d symmetry, while the t_2 orbital splits into a_1 - and e -orbital in the C_{3v} symmetry. As the energy splitting of the a_1 - and e -orbitals was small, a hole transfer took place between them, resulting in an oscillation of calculated result. Therefore, the lattice relaxation was taken into account in the same way as a nitrogen doped cluster.

Bond order for B-C bonds indicated in Fig. 5 is almost same with that calculated for C-C

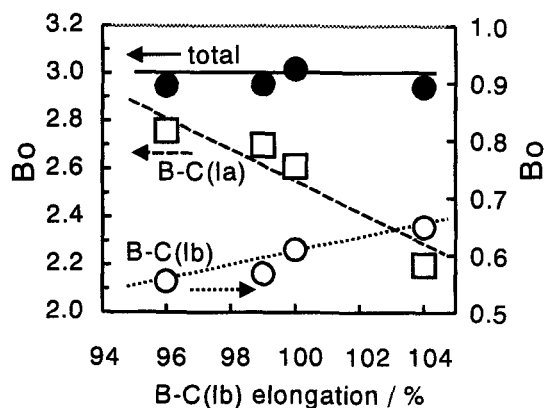


Figure 5 Relation between B_o and lattice relaxation. B_o for 100% elongation and the other were calculated for T_d and C_{3v} symmetry, respectively.

bonds in $[C_{29}H_{36}]$ cluster and larger than that of N-C bonds. This result suggests that stability of boron in diamond lattice is much higher than that of nitrogen.

From the viewpoint of B_o , the most stable position of boron in diamond could not be determined, since B_o for B-C bonds was almost independent of relaxation as indicated in Fig.5.

However, a hole located in the a_1 -orbital when a B-C(Ib) distance was shortened, while the hole located in the e -orbital when the B-C(Ib) distance was elongated. As for the cluster with elongated B-C(Ib) distance, occurrence of Jahn-Teller ($J-T$) distortion is expected, since a hole occupying doubly degenerated e -orbital. It is expected that symmetry of boron center is reduction from C_{3v} to another lower symmetry by elongation of B-C(Ib) distance.

EPR spectra for a boron center were very

broad in comparison with a nitrogen center in diamond. It was conjectured that the broadening of EPR spectra is due to dynamical $J-T$ effect or lattice relaxation.

3.3 Phosphorus Substitution

As for a P-doped diamond, converged results were obtained for both clusters in T_d

and C_{3v} symmetry. However, the electric charge of phosphorus was calculated to be positive, e.g. $+1.5e$, and independent of P-C(Ib) elongation. It was indicated that larger atomic radius of P-atom prevents the P-doping into diamond. In fact, existence of hydrogen atom in P-doped diamond has been reported[7]. Thus, it is suggested that the consideration of more complicated lattice relaxation, including cross doping effect, is necessary to discuss the electronic state of P-doped diamond.

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