n-type B-N co-doping and N Doping in diamond from first principles

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Abstract.
The boron-nitrogen (B-N) co-doped diamond with different structures have been studied by the first-principle calculations to find possible defect structures to achieve effective n-type doping. Nitrogen doped diamond itself shows the characteristics of direct bandgap, however its big gap between donor level and conduction band minimum (CBM) may contribute to its undesirable ionization energy. We found for the first time B-N co-doping as a promising method to overcome the disadvantages of N doping in diamond. B-N co-doped diamond, especially the $B-N_3$ defect, retains the characteristics of direct band gap, and has the advantages of low ionization energy and low formation energy. The effective mass of electron/ hole of B-N co-doped diamond is less than that of pure diamond, indicating better conductivity in diamond. The N-2p states play vital role in the conduction band edge of $B-N_3$ co-doped diamond. Hence, the $B-N_3$ has outstanding performance and is expected to become a promising option for N-type doping in diamond.

Keywords: B-N co-doping, n-type diamond, band structure, effective mass

1   Introduction

As an ultra-wide bandgap semiconductor material, diamond has extraordinary physical and chemical properties and is expected to be utilized in high-power electronic devices. The wide bandgap (~5.50 eV) and extreme thermomechanical properties of diamond make it a potentially vital material for future electronic devices, especially for high-frequency, high-power, high irradiation tolerant and high-temperature applications. Besides, its carrier mobility, critical breakdown field and thermal conductivity make diamond stand out from other wide-bandgap semiconductor materials.

Diamond doping has been the focus of continuous attention in the past few decades and various scientific experiments have been conducted. P-type doping in the diamond can be realized by boron doping, whose acceptor level is 0.37 eV. Wide doping range (10^{14} to 10^{21} cm^{-3}) has been realized as well[1]. However, achieving an appropriate n-type diamond is still challenging. Elements from Group I, V and VI have been studied as dopant for diamonds in recent years. Substitutional nitrogen may provide an extra electron, but its deep donor level(1.4 eV below the edge of the conduction band) limits its applications on room temperature semiconductor devices[2].Though the ionization energy of P doping is only 0.43 eV, its low carrier mobility (~23 cm/V.s) makes it unsuitable for room temperature applications as well[3]. Shallow levels cited for sulfur doping turned out to be incorrect due to inadvertent contamination with boron, and S donor level is currently believed to be closer to 1.4

eV[4]. In addition, the formation energy of sulfur is far greater than that of phosphorus (4.2 eV), indicating sulfur is more difficult to incorporate into diamond than phosphorus, and its solubility in bulk diamond will also be lower, which directly affects doping efficiency. Prins[5] obtained a shallow n-type diamond(donor level:0.32eV) through oxygen implantation. Yet, the oxygen donors would be deactivated after being annealed above 600 ℃. Interstitial Li and Na in diamond have been calculated: the donor level of interstitial Li is 0.1 eV [6] and the donor level of interstitial Na is 0.3 eV [7]. However, their solubility in diamond is extremely low and are likely to combine with other impurities or defects in diamond, leading to electrical inactivity.

Up to now, no suitable single dopant has been found to achieve the n-type shallow donor doping of diamond, especially at ionization energy and formation energy angles.

Researchers have begun to use co-doping method to study diamond impurity doping. Some experiments have achieved n-type diamond through B-S co-doping[8]. Theoretical explanations for B-S co-doping have been published[9].

However, the performance of B-N co-doped diamond is far from ideal and better explanation of co-doped diamond system is still needed to be explored. Previous work[11] has mainly studied the bond length and ionization energy of B-N clusters in diamond. There is still a lack of calculation and research on key parameters such as DOS, band structure, and carrier effective mass of B-N co-doped diamond. Hence, it is necessary to explore the conductivity mechanism of B-N co-doped diamond with shallow donor level.

2   Calculation Methods

This paper follows the calculation method in our previously published work[9]-[10]. All calculations were performed based on density functional theory (DFT) to optimize the geometric structure and compute the band structure and density of state. The exchange-correlation function is implemented by VASP through the Perdew–Burke–Ernzerhof (PBE) within generalized gradient approximation (GGA) [1] Projector augmented plane-wave (PAW) potentials is chosen to describe the core-valence interaction. In this research, the cutoff energy of plane-wave was set to 500 eV using convergence verification [12], the convergence criterion of electronic structure relaxation calculation was set as 1×10^{-5} eV, and the convergence criterion of the inter-atomic forces was set as 1×10-4 eV/Å. A 216-atom supercell ($3\times3\times3$) of diamond, with a $9\times9\times9$ mesh (Monkhorst-Pack) of KPOINTS was adopted for the calculation. A large cell size was essential to ensure the reliability of calculation results, especially for shallow doping studies. The bulk diamond's lattice constant was converged to 3.573 Å, in line with previous experiments, and was served as the original building block for supercell construction.

3 Results and discussion

3.1 Impurity formation energy(Ef)

The impurity formation energy is calculated to judge the possibility and stability of impurity doping into the material. The lower the value, the easier and more stable the impurity doping is, which is conducive to effective doping.

The formation energy of impurity X in charge state q is defined as:

$$E_f [Xq] = E_{tot} [Xq] - E_{tot} [C,bulk] - \sum nX \mu X - q(E_F + \Delta V) \tag{1}$$

where Etot[Xq] denotes the total energy of the whole structure and Etot[C,bulk] denotes the total energy of the perfect diamond bulk without any impurity. nX describes the number of doping/removing impurity atoms of atom X (C atoms or doping atoms), μX denotes the chemical potential of impurity X. In this study, the chemical potential of nitrogen was calculated from N_2 and the chemical potential of boron was from B_2H_6[13]. E_F denotes the Fermi level referenced to the VBM (Ev), and ΔV is an alignment of electrostatic potentials between the defect supercell and the bulk. In this study, we primarily concentrate on the neutral charge state, which means that the value of the last term in the expression is basically zero.

The solubility of impurity is strongly related to $N\exp(-E_f/kT)$, where k is Boltzmann's constant, E_f represents the formation energy of the impurity, T denotes the temperature, and N represents the density of sites in the bulk where the impurity may incorporate [14]. Hence, the impurity solubility is strongly associated with its formation energy. A smaller formation energy usually indicates better doping efficiency.

First, we investigated the formation energy of a nitrogen atom or boron atom in diamond at substitutional site or interstitial site. As shown in Table 1, the formation energy of substitutional boron atom (or substitutional nitrogen atom) doped diamond is significantly lower than that of interstitial nitrogen/boron atom doped diamond, suggesting that substitutional sites of nitrogen and boron atoms are easier to be incorporated. Therefore, we focus on the substitutional doping when studying B-N co-doped diamond.

Table 1. Impurity formation energy (E_f) of interstitial B (B_i), substitutional B (B_s), interstitial N (N_i), and substitutional N (N_s) doping in diamond

Compound	Position	E_f /eV
$C_{215}N$	N_s	2.127
$C_{216}N$	N_i	8.869
$C_{215}B$	B_s	-0.257
$C_{216}B$	B_i	5.675
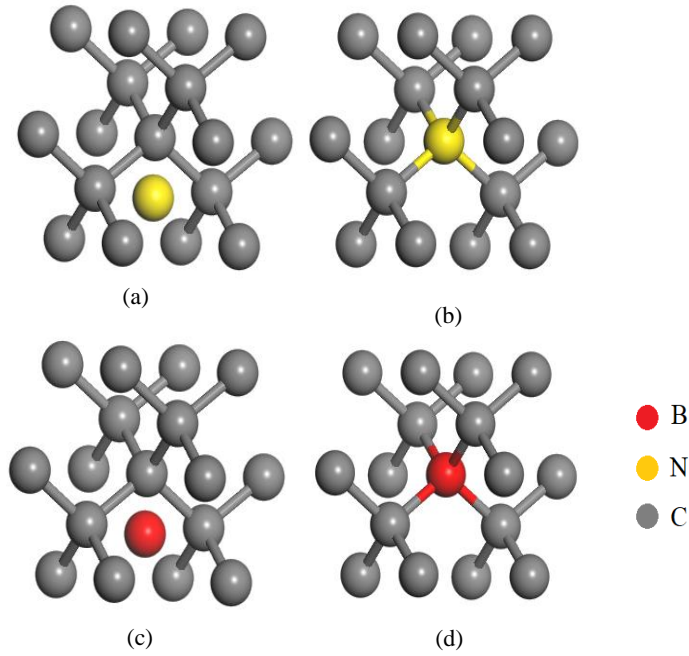
Fig. 1. Doping structure of interstitial nitrogen(a), substitutional nitrogen(b), interstitial boron(c), substitutional boron(d).
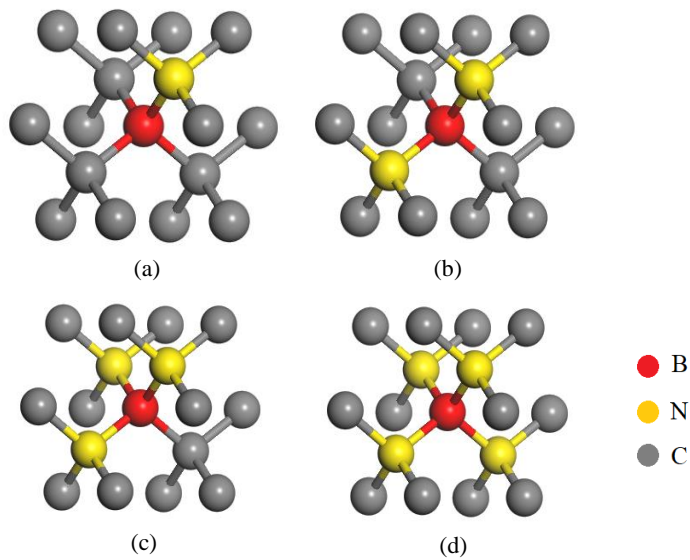
Fig. 2. Doping structures of B-N$_1$ (a), B-N$_2$ (b), B-N$_3$ (c), and B-N$_4$ (d).

The covalent radius of nitrogen (0.734 Å) and boron (0.82 Å) are close to that of carbon (0.77 Å), indicating much lighter lattice distortion than other substitutional dopants. Smaller lattice distortion results in less internal strain, which contributes to the construction of doped structures with low formation energy.

Multiple nitrogen atoms were added around the substitutional boron atom to replace those original nearest neighbor carbon atoms. Fig. 2 demonstrates the four structures mainly studied in this paper, which are a substitutional boron atom connected with one to four neighboring nitrogen atoms. The formation energies of the four structures are shown in Table 2.

Calculation results in Table 2 distinctly illustrate that the formation energies of the four structures are low, which are -1.662 eV, -1.257 eV, -0.875 eV, and 0.523 eV. The formation energies of other common dopants, such as S(11.1eV), P (10.4 eV) and B-S (6.2 eV) are much greater. The low formation energy suggests great potential for effective doping.

The low formation energies of these impurities indicate that nitrogen and boron atoms exist as a whole in the diamond instead of as individual dopants. Therefore, its electrical properties shall not be explained by the traditional compensation effect.

Table 2. Impurity formation energy (Ef) of B-N co-doped diamond with different structures.

Compound	Structure	Ef/eV
$C_{214}B_1N_1$	$B-N_1$	-1.662
$C_{213}B_1N_2$	$B-N_2$	-1.257
$C_{212}B_1N_3$	$B-N_3$	-0.875
$C_{211}B_1N_4$	$B-N_4$	0.523

3.2 Band Structure
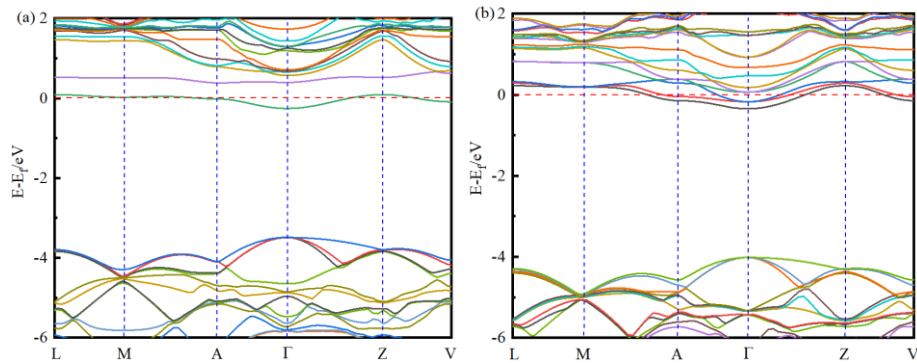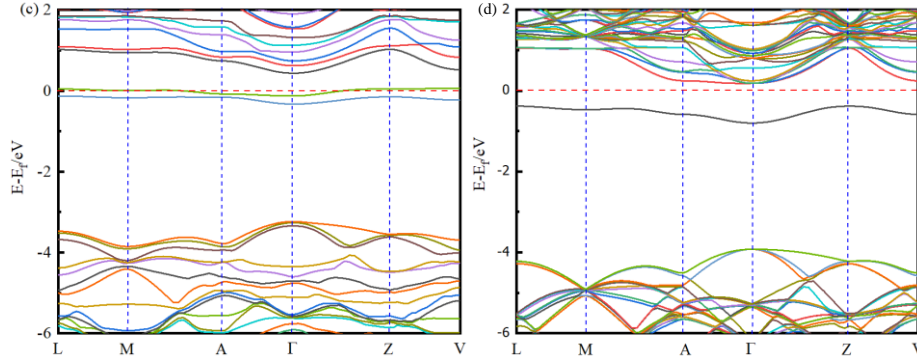
Fig. 3. Band structures of doped diamond with B-N_2 (a), B-N_3 (b), (c) B-N_4, and (d)Nitrogen

We conducted in-depth research and analysis on N doping and B-N doping in diamond. The band structures of n-type diamond formed by nitrogen doping and B-N co-doping are shown in Figure 3. The band structures of nitrogen doped and B-N co-doped led n-type diamond are shown in Fig. 3. In comparison with the pure diamond, the nitrogen, B-N_2, B-N_3, and B-N_4 doped diamonds indicate credible n-type conductivity in that those conduction band minimums (CBM) are close to fermi energy level and the intermediate band (IB) in the bandgap can be regarded as the donor energy level. As shown in Fig. 3, the valence band maximum (VBM), conduction band minimum (CBM) and the intermediate band (IB) minimum of nitrogen doped diamond are at the same k-point, suggesting a direct bandgap is formed, hence, enhancing the optical and electronic properties. Therefore, nitrogen doped diamond itself has the characteristics of direct band gap. However, the donor level of nitrogen doped diamond is far from the conduction band minimum (CBM), which may be the major reason for undesirable electrical properties of N doped diamond. B-N co-doping is a promising technique that overcomes the disadvantages of N doped diamond, especially in the field of ionization energy. B-N co-doped diamond preserves the characteristics of the direct band gap and significantly reduces the gap between the donor level and the conduction band minimum (CBM). B-N_3 doped diamond seems to be the most promising defect structure, since there is no obvious gap between the donor level and the CBM, in other words, there is no apparent intermediate level. The novel characteristic may indicate great potential for better ionization energy performance. As far as we know, this is the first time these results have been reported. B-N co-doped diamond is expected to have outstanding electrical and optoelectronic properties.

Furthermore, we calculated the electron effective masses of diamond with B-N_2, B-N_3, and B-N_4 doped. The calculation results of electron effective masses are presented in Table 3. In order to ensure the accuracy of the calculation results, we also calculated the effective mass of pure diamond (longitudinal and transverse), and the calculated results are in good agreement with the experimental results. The electron's effective masses of B-N co-doped diamond is basically smaller than pure diamond.

Table 3. Electron's effective masses of diamond co-doped with B-N and pure diamond.

Structure	Direction	Effective masses （m_0）	Reports
B-N_2	(100)	0.34	
B-N_2	(111)	0.35	
B-N_3	(100)	0.26	
B-N_3	(111)	0.26	
B-N_4	(100)	0.45	
B-N_4	(111)	0.57	
Pure Diamond (longitudinal)	(100)	1.52	1.4[25],1.56[26]
Pure Diamond (transverse)	(100)	0.38	0.36[25],0.28[26]

3.3 Ionization energies

The thermodynamic transition level $\varepsilon(q_1,q_2)$ can be determined by equation(2) [15-16]:

$$\varepsilon(q_1,q_2) = \frac{E_{tot}\left[X^{q_1}\right] - E_{tot}\left[X^{q_2}\right]}{q_2 - q_1} - E_V - \Delta V$$

(2)

where $Etot[X^{q1}]$ and $Etot[X^{q2}]$ denote the total energy of the whole structure including the defect X with charge states. E_V and ΔV are consistent with the meaning in the previous formula (1). The acceptor ionization energy E_A is equal to the transition level $\varepsilon(0/-)$, and the donor ionization energy E_D equals Eg minus $\varepsilon(0/+)$[17], where Eg equals the bandgap of pure diamond calculated by VASP(4.1 eV).

To ensure the correctness of our calculation results, we calculated some doping results already verified in experiments and other theoretical calculations. Our calculation results are shown in Table 4, consistent with previous theoretical and experimental results.

Table 4. Ionization energies (E_D, eV) of some n-type dopants in diamond.

Dopant	E_D /eV(Our work)	E_D/eV(Ref.)
P	0.59	0.43[b]-0.56[a][3][19]
S	1.44	1.4 [b] [4]
O	0.45	0.32[b][5]
N	1.43	1.4[a,b][2][21]
Li(interstitial)	0.04	0.1[a][7]
BS	0.55	0.39[a]-0.52[b][22][23]
Li-N_4	0.232	0.271[a][24]

[a] Theoretical values [b] Experimental values

Table 5. Ionization energies (E_D, eV) and formation energy(E_f, e) of n-type B-N co-doped defects in diamond

Dopant	E_D /eV	E_f /eV
B-N_2	0.63	-1.257
B-N_3	0.23	-0.875
B-N_4	0.54	0.523

The donor ionization energies (E_D) of B-N co-doping dopants are listed in Table 5. It is apparent that BN_2, BN_3, and BN_4 demonstrated n-type diamond characteristics with low donor levels. The donor ionization energy of BN_3 is 0.23 eV, which is the best performer in our research.

Our ionization energy calculation results are not quite consistent with previous research[11], in which BN_2, BN_3, and BN_4 have larger ionization energies(greater than 1eV). This may be due to different calculation methods . In the previous article, the ionization energy was obtained by the difference between the CBM and the impurity energy level, while we calculated the ionization energy by formula (2). We believe that the calculation method of the previous work is not accurate enough, and the method we adopt is a widely used calculation method, thus, the calculation results are more credible.

3.4 Electronic Structure

We calculated the total density of states (TDOS) of B-N_2, B-N_3, and B-N_4 co-doped diamond, and the results are displayed in Fig. 4. As shown in Fig. 4, the impurity level and fermi level of B-N_2, B-N_3, and B-N_4 are near the conduction band minimum (CBM). According to the calculation results of the band structure, it is evident that the B-N co-doping can achieve n-type diamond doping, which are in line with the previous discussion of ionization energy. Together, the calculation results of these two parts verify that B-N_2, B-N_3, B-N_4 co-doped diamonds are n-type diamonds.

Combining the performances of TDOS, ionization energy, and formation energy, we assume B-N_3 co-doping as a very promising defect structure to realize shallow n-type doping in diamond. We calculated the partial densities of state (PDOS) of B-N_3 for in-depth knowledge of its donor characteristics. As shown in Fig. 5, N-2p states play decisive role in the conduction band edge.

Based on previous calculations and discussions, the performance of B-N_3 doping is extremely outstanding, and it has negative formation energy and extremely low ionization energy. Other B-N co-doped structures can also achieve N-type diamond doping. B-N_3 has strong stability in diamond, is easy to form effective doping, and has a shallow donor energy level. Therefore, it can be concluded that B-N_3 co-doping may be a promising alternative to achieve n-type doping with shallow donor levels in diamond.
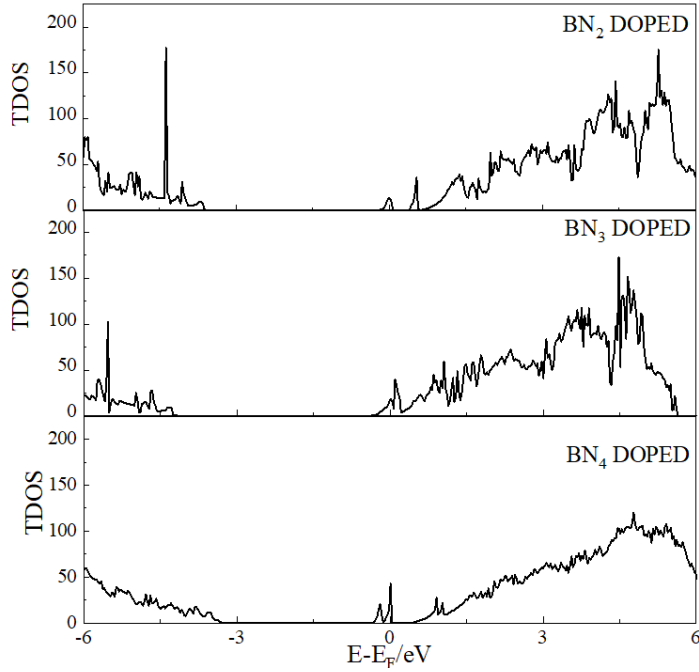
Fig. 4. TDOS of the B-N₂, B-N₃, B-N₄ doped diamond.
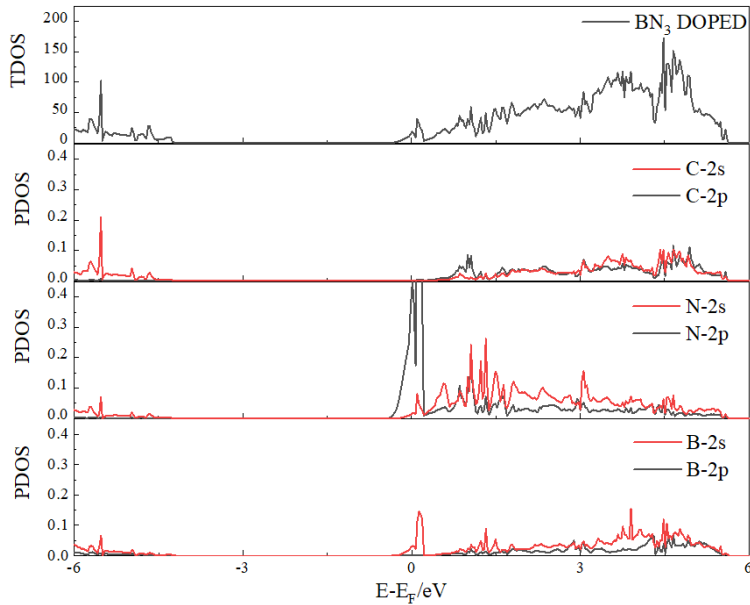
Fig. 5. TDOS and PDOS of the B-N₃-doped diamond. (a) TDOS of the B-N₃-doped diamond; PDOS of the B-N₃-doped diamond for (b) C atoms, (c) N atoms, (d) B atom.

4 Conclusions

In conclusion, B-N co-doped can be expected to realize desirable n-type diamond. B-N3 co-doped diamond has the advantage of low formation energy(-0.875eV) and low ionization energy(0.23eV), indicating great potential for effective doping and shallow n-type doping. Besides, we found that the valence band maximum (VBM), the intermediate band (IB) minimum and covalent band maximum (CBM) of boron and nitrogen co-doping diamond are at the same k-point, which contrasts with pure diamond. N-2p states mainly determine the conduction band edge of B-N$_3$ doped diamond, suggesting the incorporated nitrogen atoms play crucial role in conductivity besides improvement in effective doping. Our study demonstrates that the B-N$_3$ structure has the merit of shallow donor level and high solubility, thus, it can be seen as a promising alternative for n-type diamonds. Our calculation results need to be further verified by experiments.

References

1. Czelej K , Spiewak P , Kurzydowski K J . Electronic Structure and N-Type Doping in Diamond from First Principles[J]. Mrs Advances, 2016, 1(16):1093-1098.
2. Shah Z M , Mainwood A . A theoretical study of the effect of nitrogen, boron and phosphorus impurities on the growth and morphology of diamond surfaces[J]. Diamond & Related Materials, 2008, 17(7-10):1307-1310.
3. B, Hiromitsu Kato A , et al.Diamond bipolar junction transistor device with phosphorus-doped diamond base layer[J]. Diamond and Related Materials, 2012, s 27–28:19-22.
4. Sque S J , Jones R , Goss J P , et al. Shallow donors in diamond: chalcogens, pnictogens, and their hydrogen complexes.[J]. Physical Review Letters, 2004, 92(1):017402.
5. Prins J F . n-type semiconducting diamond by means of oxygen-ion implantation[J]. Physical Review B, 2000, 61(11):7191-7194.
6. S, A, Kajihara, et al. Nitrogen and potentialn-type dopants in diamond[J]. Physical Review Letters, 1991, 66(15):2010–2013.
7. Theoretical study of Li and Na as n-type dopants for diamond[J]. Physical Review B, 2007, 75(7):2978–2984.
8. Eaton S C , Anderson A B , Angus J C , et al. Co-doping of Diamond with Boron and Sulfur[J]. Electrochemical and Solid-State Letters, 2002, 5(8):G65.
9. Tang, Lin, Yue, et al. N-type B-S co-doping and S doping in diamond from first principles[J]. Carbon: An International Journal Sponsored by the American Carbon Society, 2018, 130:458-465.
10. D Zhou, Tang L , Geng Y , et al. First-principles calculation to N-type Li N Co-doping and Li doping in diamond[J]. Diamond and Related Materials, 2020, 110:108070.
11. Croot A , Othman M Z , Conejeros S , et al. A theoretical study of substitutional boron-nitrogen clusters in diamond[J]. Journal of Physics Condensed Matter, 2018, 30(42).
12. Chadi, D . J . Special points for Brillouin-zone integrations[J]. Physical Review B, 1977, 16(4):1746-1747.
13. Spiewak, Piotr, Kurzydlowski, et al. Electronic structure of substitutionally doped diamond: Spin-polarized, hybrid density functional theory analysis[J]. Diamond & Related Materials, 2017.Walle V D , Chris G . First-principles calculations for defects and impurities: Applications to III-nitrides[J]. Journal of Applied Physics, 2004, 95(8):3851-3879.

14. Ullah, M. , Ahmed, E. , Hussain, F. , Rana, A. M. , Raza, R. , & Ullah, H.. "Electronic structure calculations of oxygen-doped diamond using DFT technique."Microelectronic Engineering 146.OCT.1(2015):26-31.

15. Freysoldt C , Grabowski B , Hickel T , et al. First-principles calculations for point defects in solids[J]. Review of Modern Physics, 2014, 86(1).

16. Walle V D , Chris G . First-principles calculations for defects and impurities: Applications to III-nitrides[J]. Journal of Applied Physics, 2004, 95(8):3851-3879.

17. Goss, J. P. , P. R. Briddon , and R. J. Eyre . Donor levels for selected n-type dopants in diamond: A computational study of the effect of supercell size. Physical Review B Condensed Matter & Materials Physics, 2006,74.24(2006):p.245217.1-245217.7.

18. Koizumi S , Kamo M , Sato Y , et al. Growth and characterization of phosphorous doped {111 homoepitaxial diamond thin film[J]. The FASEB Journal, 1997, 9(8):651-658.

19. A, Takehide Miyazaki , and H. O. B .A theoretical study of a sulfur impurity in diamond[J]. Diamond and Related Materials, 2001, 10(3–7):449-452.

20. Moussa, J. E. , Marom, N. , Sai, N. , & Chelikowsky, J. R.. "Theoretical Design of a Shallow Donor in Diamond by Lithium-Nitrogen Codoping." Physical review letters 108.22(2012）:p.226404.1-226404.5.

21. Schwingenschloegl U , Chroneos A , Schuster C , et al. Doping and cluster formation in diamond[J]. Journal of Applied Physics, 2011, 110(V110N5):162.

22. Jing Z , Li R , Wang X , et al. Study on the Microstructure and Electrical Properties of Boron and Sulfur Codoped Diamond Films Deposited Using Chemical Vapor Deposition[J]. Journal of Nanomaterials, 2014, 2014(21):4338-4346.

23. Eaton S C , Anderson A B , Angus J C , et al. Diamond growth in the presence of boron and sulfur[J]. Diamond & Related Materials, 2003, 12(10-11):1627-1632.

24. Moussa, J. E. , Marom, N. , Sai, N. , & Chelikowsky, J. R.. "Theoretical Design of a Shallow Donor in Diamond by Lithium-Nitrogen Codoping." Physical review letters 108.22(2012）:p.226404.1-226404.5.

25. F. Nava, C. Canali, C. Jacoboni, et al., Electron effective masses and lattice scattering in natural diamond, Solid State Commun. 33 (4) (1980) 475-477.

26. N. Naka, K. Fukai, Y. Handa, et al., Direct measurement via cyclotron resonance of the carrier effective masses in pristine diamond, Phys. Rev. B 88 (3) (2013), 035205.