First-Principles Calculation to N-type Beryllium related Co-doping and Beryllium Doping in Diamond

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Abstract. The Beryllium-doped (Be-doped) diamond and Beryllium related (Be-X) co-doped diamond have been carefully investigated by the density functional theory (DFT) to explore the possibility to achieve effective and shallow n-type doping in diamond. Although the ionization energy and formation energy of interstitial/substitutional Be-doped diamond is not ideal, the introduction of Be-related co-doping techniques(Be-N/O/S) greatly improves the electrical properties in diamonds. We found, for the first time, n-type diamond doping can be realized in Be-N, Be-O and Be-S co-doped systems, among which Be-N_3 has the best performance. Be-N3 has the advantages of low ionization energy(0.25eV) ,low formation energy(-1.59eV), and direct bandgap. The N-2p states play a crucial role in the conduction band edge of Be-N3 co-doped diamond. Hence, the Be-N_3 could be expected to become a promising alternative for N-type shallow doping in diamond

Keywords: Beryllium-related Co-doping, First-principles Calculation, Diamond.

1   Introduction

Diamond has been extensively studied due to its outstanding properties since the end of the last century. Diamond is not only a superhard material for mechanical cutting, but also a semiconductor material with full potential, and it is even expected to become the ultimate semiconductor material. Diamond has large bandgap(5.5eV)[1], unparalleled thermal conductivity(22 W/cm·K)[2], and its electric breakdown field(10 MV/cm)[3] and carrier mobility(4500 cm^2 /Vs for electrons[4]; 3800 cm^2 /Vs for holes[5]) show obvious advantages compared with other semiconductor materials. These unique properties make it a promising option to be used in novel electronic device, especially in the field of high temperature, high pressure and high power.

Although diamond material has tremendous advantages, a series of fundamental problems remain to be resolved. In addition to the immense difficulty of growing large-scale single crystal diamonds, achieving effective diamond doping is one of the most significant obstacles. In order to construct basic diamond electronic devices, it is necessary to solve the n-type and p-type doping of diamond. At present, the p-type doping of diamond has been basically solved through boron doping[6], however, the problem of

n-type doping has not been properly resolved. Diamond n-type doping requires the introduction of appropriate dopants to achieve effective shallow doping. Currently, research on n-type diamond doping can be mainly divided into single element doping and co-doping. The research of single doping includes interstitial doping of the first group elements (Li, Na)[7-8] and the substitutional doping of the fifth and sixth group elements (N, P, O, S)[9-13]; co-doping includes Li-N[14], B-S[15], Li-P[16],B-N[17-18]in diamond. Although the formation energy of B-S co-doping is lower than that of sulfur doping, it is still relatively high. Li-N co-doping has outstanding performance but due to the existence of barrier energy, the progress in experimental preparation is slow. Though researchers all over the world have made continuous attempts and efforts, there is no recognized technical route to achieve ideal diamond N-type doping yet. Therefore, exploring the method of realizing n-type doping in diamond is the focus of current research.

Other second-period elements in the periodic table (Li, B, N, O)[6,7,9,12] have been extensively studied in diamond doping. Beryllium element, which is also in the second period, also has research potential due to its close atomic radius to C atom. Beryllium-doped diamond has been successfully prepared by MPCVD method in experiments[19], proving the feasibility of incorporating beryllium into diamond. However, there is no theoretical/experimental research on beryllium and other elements co-doped diamond research, investigations on Be-related co-doping on the realization of N-type diamond doping is still rare, worthy of in-depth research.

In this article, we calculated the doping of beryllium in diamond and managed to achieve excellent performance of diamond n-type doping by co-doping Beryllium and other elements (Nitrogen, Oxygen, and Sulfur). We systematically calculated the formation energy, ionization energy, band structure, density of states(TDOS and PDOS) of these structures to carefully analyze the electrical properties of these structures, and finally found that some beryllium co-doped structures may have outstanding performance.

2   Calculation Methods

This publication follows the same computational methodology as our earlier work [14, 15, 17]. All calculations are done using density functional theory (DFT) to optimize the geometry, calculate the density of states (DOS), and determine the band structure. VASP through Perdew-Burke-Ernzerhof (PBE) are implemented to perform exchange-correlation function within the generalized gradient approximation (GGA). [20] Projected augmented plane wave (PAW) potentials are employed to describe core-valence interactions. In this study, the cut-off energy of the plane wave is set to 500 eV. the convergence criterion of the electronic structure relaxation calculation is set to 1×10^{-5} eV, and its criterion of the interatomic force is adjusted to 1×10^{-4} eV after the convergence verification [21]. For calculations, the 216-atom supercell of diamond ($3\times3\times3$) and the Monkhorst-Pack grid of KPOINTS ($9\times9\times9$) are employed. Larger cell sizes are

deemed essential to guarantee the reliability of output results, particularly for shallow doping studies in diamond. The atomic positions where the lattice constant of bulk diamond converges to 3.573 Å. We found that result was consistent with previous studies [23]

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 in the doped diamond $E_f[X^q]$ is defined as[24]:

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

where $E_{tot}[X^q]$ is the total energy of the whole structure including the charged dopant X and $E_{tot}[C_{,bulk}]$ is the total energy of the perfect diamond bulk. n_X is denoted as the number of atom of element X (host atoms or impurity atoms) that has been added to ($n_X > 0$) or removed ($n_X < 0$) from the supercell to form the defect. μ_X is the chemical potential of impurity X, and the summation is conducted when various impurities co-exist in the supercell at the same time. In this paper, we investigate the chemical potential of Beryllium from the hexagonal close-packed structure of pure Be bulk, while the chemical potential of Oxygen is based on O_2, Sulfur from H_2S, and Nitrogen from NH_3. In addition, E_F is the Fermi level of the doped diamond, and we assume the ΔV as a correction term to unify the electrostatic potentials between the diamond bulk and the supercell with impurities. In the following analysis, we would focus on the neutral charge state of the impurity and therefore, the last term is zero.

The impurity solubility is proportional to $N\exp(-E_f/kT)$, where E_f represents the impurity formation energy, k denotes the Boltzmann's constant, T denotes the temperature, and N denotes the density of states in the supercell that the dopant atom occupies. Therefore, the solubility is strongly correlated to the formation energy. Smaller formation energy indicates better doping effectivity.

We first calculated the formation energies of Be interstitial doping(Be_i) and Be substitutional doping(Be_s). The formation energies of Be_i and Be_s are 10.07eV and 4.81eV. Similar to the doping of the first group elements (Li, Na), the formation energy characteristics of Be doping alone are not ideal. Due to its high formation energy, it can be concluded that Be's solid solubility is low, and it is difficult to achieve effective doping by directly incorporating Be into the diamond.

Co-doping in diamond may cause smaller lattice distortion, thereby reducing the impurity formation energy. Therefore, we tried to co-dope Be with other element atoms into the diamond. We calculated the formation energy of BeX_n (X denotes N, S, O, n=1~4) in a supercell, where Be occupies the position of the original carbon atom in a diamond structure in the form of substitution, and the X element atoms replace those carbon atoms that are nearest neighbors of the central Be atom.

As shown in Table 2, some Be-X_n (X denotes N, O, S, n=1~4) structures have a smaller formation energy than Be single doping, that is, the co-doping method is effective for reducing the formation energy of Be impurities in diamonds. The formation energy of Be-S co-doped diamond is generally higher. One possible explanation is that the atomic radius of sulfur atoms is larger (much larger than that of nitrogen and oxygen atoms), and the lattice distortion caused by the co-doped structure is correspondingly larger. The formation energy of Be-N_3 and Be-N_4 is comparatively low, which are -1.59eV and -1.42eV accordingly. In general, the formation energy of Be-O co-doping is lower than Be-S co-doping but higher than Be-N co-doping, and it is better than most single-doping structures in terms of defect formation energy.

The length of the C-C bond in the pure diamond structure is 1.54Å, which is smaller than those of the C-Be bond in substitutional Be doped (1.68Å). The reason for the longer C-Be bond length may be due to the larger radius of Be atoms, which squeezes the surrounding C atoms to the outside after incorporation. Selecting the structure with the lowest formation energy under each co-doping system, we found that the distance of the Be-S bond is 1.79Å, the Be-O bond is 1.61Å, and the Be-N bond is 1.64Å. The bond length and the internal lattice distortion are related to the defect formation energy. Generally speaking, the larger the lattice distortion is, the longer the bond length is, and the larger the impurity formation energy is. The combination of bond length and impurity formation energy of Be-Xn (X denotes N, S, O, n=1~4) is consistent with the above theory, and also verifies that Be-N co-doping is the result of better performance in Be-X_n co-doping structures in diamond.b
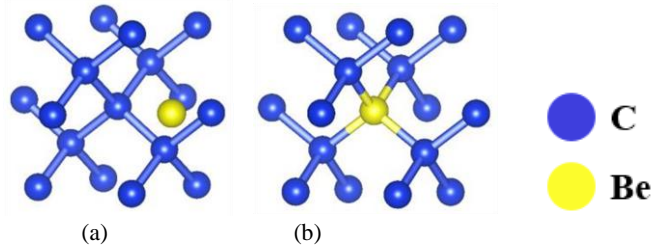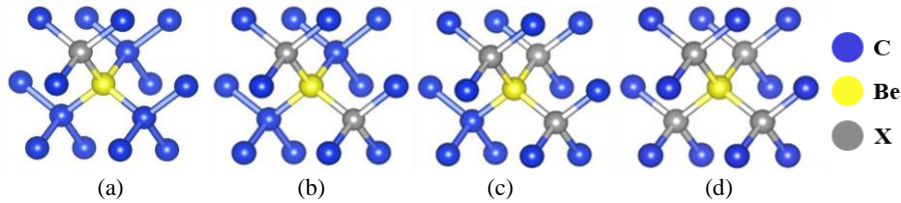

FIG. 1. The doping structures of Be_i (a), Be_s (b).

FIG. 2. The doping structures of Be-X_1 (a), Be-X_2 (b), Be-X_3 (c), and Be-X_4 (d).

Table 1. Impurity formation energy (E_f) of interstitial Be (Bei), substitutional Be (Bes), and Be-related dopants in diamond

Compound	Position	E_f /eV
$C_{216}Be$	Be_i	10.08
$C_{215}Be$	Be_s	4.81
$C_{214}Be_1N_1$	$Be-N_1$	1.57
$C_{213}Be_1N_2$	$Be-N_2$	-1.38
$C_{212}Be_1N_3$	$Be-N_3$	-1.59
$C_{211}Be_1N_4$	$Be-N_4$	-1.42
$C_{214}Be_1O_1$	$Be-O_1$	3.30
$C_{213}Be_1O_2$	$Be-O_2$	4.72
$C_{212}Be_1O_3$	$Be-O_3$	5.79
$C_{211}Be_1O_4$	$Be-O_4$	8.45
$C_{214}Be_1S_1$	$Be-S_1$	7.23
$C_{213}Be_1S_2$	$Be-S_2$	11.41
$C_{212}Be_1S_3$	$Be-S_3$	14.74
$C_{211}Be_1S_4$	$Be-S_4$	18.67

3.2 Ionization energies

Ionization energy is a key parameter for judging the performance of doping. The lower the ionization energy, the easier it is to be activated. In this paper, the thermodynamic transition level ε(q1,q2) is adopted to estimate the ionization energy with the PBE methods. The equation of thermodynamic transition level is provided as follows[25]

$$\varepsilon(q_1, q_2) = \frac{E_{tot}\left[X^{q_1}\right] - E_{tot}\left[X^{q_2}\right]}{q_2 - q_1} - E_V - \Delta V \tag{2}$$

where the connotation of $E_{tot}[X^{q_1}]$ and $E_{tot}[X^{q_2}]$ are consistent with the previous part of formation energy. E_V is the valence band maximum of the pure diamond. The transition level $\varepsilon(0/-)$ is equal to the ionization energy(acceptor level) E_A, and the ionization energy of the donor is $E_D = E_g - \varepsilon(0/+)$[26], where E_g is the DFT calculation bandgap of pure diamond of 4.1eV.

We have verified the correctness of our calculation results by calculating the structure of some existing experimental/theoretical results and comparing them with our own results(Table 2).

The ionization energies of Be-doped (substitutional and interstitial) and Be-co-doped diamond calculated according to the formula are shown in Table 3.

Substitutional Be-doped diamond is a p-type semiconductor, while interstitial Be-doped diamond is n-type. The ionization energy of interstitial Be-doped

semiconductors is xx, which is better than N single-doping and S single-doping, and not as good as Na and Li single-doping. Part of the Be-related co-doped structure can achieve n-type doping. BeN_3 and BeN_4 in the Be-N co-doped system, BeO_2, BeO_3, BeO_4 in the Be-O co-doped system, and BeS_2, BeS_3, BeS_4 in the Be-S co-doped system may have donor energy levels. The ionization energies of BeN_3, BeO_2, and BeS_2 structures are 0.25eV, 0.86eV, and 0.56eV, respectively, the best in each co-doped system. Combined with the previous calculation results of impurity formation energy, we believed that BeN_3, BeS_2, and BeO_2 are the structures with outstanding performance among Be-related co-doped structures, worthy of more in-depth exploration.

Table 2. Ionization energies 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][10][27]
S	1.44	1.4 [b] [11]
O	0.45	0.32[b][12]
N	1.43	1.4[a,b][7][28]
Li(interstitial)	0.04	0.1[a][8]
BS	0.55	0.39[a]-0.52[b][29][30]
Li-N_4	0.232	0.271[a][31]

[a] Theoretical values [b] Experimental values

Table 3. Ionization energies (eV) of Be-related co-doped defects in diamond

Dopant	E_D /eV
Be_i	1.76eV(E_D)
Be_s	1.16eV(E_A)
Be-N_1	0.68 eV(E_A)
Be-N_2	0.43 eV(E_A)
Be-N_3	0.25 eV(E_D)
Be-N_4	0.33 eV(E_D)
Be-O_1	0.77 eV(E_A)
Be-O_2	0.86 eV(E_D)
Be-O_3	0.91 eV(E_D)
Be-O_4	0.88 eV(E_D)
Be-S_1	0.62 eV(E_A)
Be-S_2	0.56 eV(E_D)
Be-S_3	0.71 eV(E_D)
Be-S_4	1.03 eV(E_D)

E_D refers to the donor level of n-type semiconductor
E_A refers to the acceptor level of p-type semiconductor

3.3   Electronic Structure

We performed further calculation and analysis on Be doping and Be-related co-doping in diamond. As shown in the Fig.3, the substitutional Be-doped diamond demonstrated p-type characteristics with an acceptor level. The Fermi level of interstitial Be-doped diamond is close to the bottom of the conduction band, indicating n-type diamond characteristics. These calculation results are consistent with the ionization energy calculation results above.

Combined with the previous results of formation energy and ionization energy, we further calculated the structures with better performance in various co-doped systems. We investigated the total density of states (TDOS) of $Be-N_3$, $Be-S_2$, and $Be-O_2$ co-doped diamond, and the partial density of states (PDOS) of $Be-N_3$ so as to identify their donor properties. The calculation results (TDOS and PDOS) are displayed in Fig. 3 and Fig. 4. According to our calculation results, the Fermi level of $Be-N_3$, $Be-S_2$, and $Be-O_2$ doped diamond is close to the conduction band minimum (CBM). These results are in agreement with those of previous band calculations. The mutually corroborated calculation results prove that these structures are capable of N-type diamond doping.

Among Be co-doped diamonds, the performance of the Be-N co-doped system is more advantageous, and after further comparative analysis, BeN_3 has the most outstanding performance, since its properties of low formation energy and low ionization energy at the same time. The atomic radii of Be and N atoms are the closest to C atoms, and the lattice distortion caused by doping is the smallest, which may be a possible explanation of the calculation results.

Calculation results shown in Fig.4, demonstrate that N-2p states play a crucial role in the conduction band edge of $Be-N_3$ doped diamond, which explains the reason why $Be-N_3$ could achieve n-type diamond doping. Co-doped atoms not only lower the formation energy of impurity (Be) but are also a decisive factor for the realization of n-type doping. According to the calculation results of the TDOS/PDOS, it is evident that these Be-related co-doping can achieve n-type diamond doping, which are consistent with the previous discussion of ionization energy and band structure.
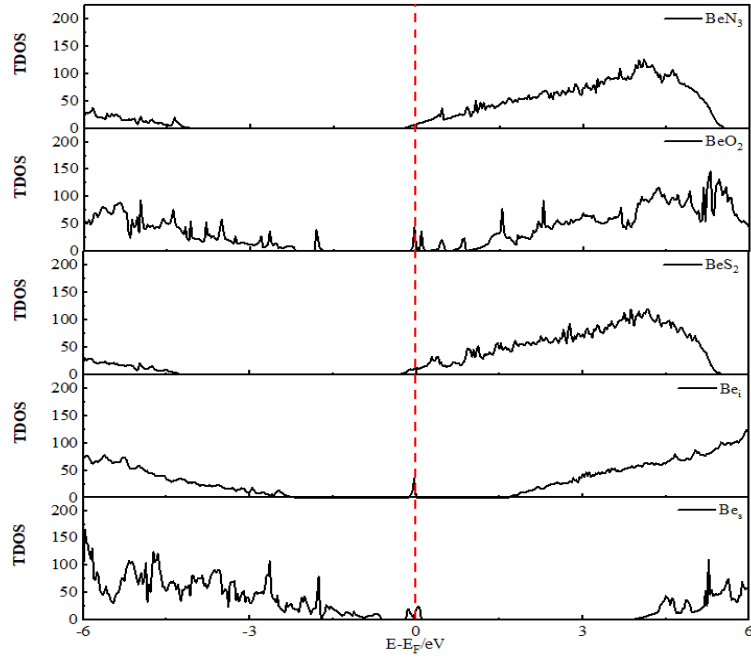
Fig. 3. TDOS of the Be-N$_3$, Be-O$_2$, Be-S$_2$, Be$_i$, and Be$_s$ doped diamond.
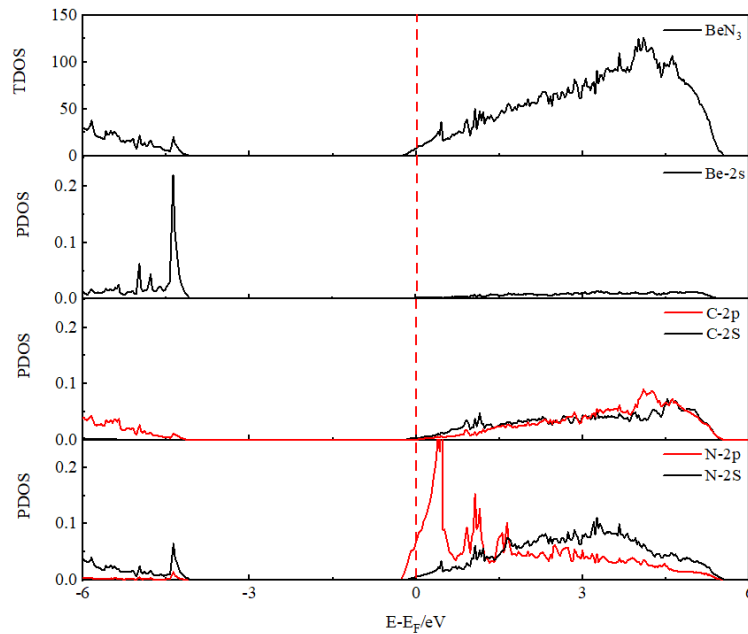

Fig. 4. TDOS and PDOS of the Be-N$_3$-doped diamond. (a) TDOS of the Be-N$_3$-doped diamond; PDOS of the Be-N$_3$-doped diamond for (b) Be atoms, (c) C atoms, (d) N atom.

3.4 Band Structure

We have calculated the band structure of a series of Be co-doped diamond, mainly for those with better performance in each co-doped system. While credible n-type doping is achieved through these doping structures, conduction band minimums (CBM) vary dramatically. As is shown in Fig.5, the CBM structure of Be-N_3 and Be-S_2 doped diamond is clear, which is consistent with the CBM of typical n-type semiconductors. However, the CBM structure of Be-O_2 doped diamond is relatively complex, in which the intermediate energy level and CBM almost overlap, which is also consistent with the results of DOS calculations.

It is worth noting that Be-X doping has a direct band gap, which is very different from pure diamond and also different from traditional single-doped diamond. The conduction band minimums (CBM), and valence band maximums (VBM) in this structure are all on the same KPOINTS, which is the characteristic of direct bandgap semiconductor. There is doubt that the band structure can be more precisely calculated by using non-local hybrid functionals of HSE06 [6]. However, given the limited calculation resources, standard PBE functional was adopted in our research. Although it underestimates the bandgap of diamond, its negative effects on the energy difference of charge state are not evident, and our analysis of formation energy is not affected as well.
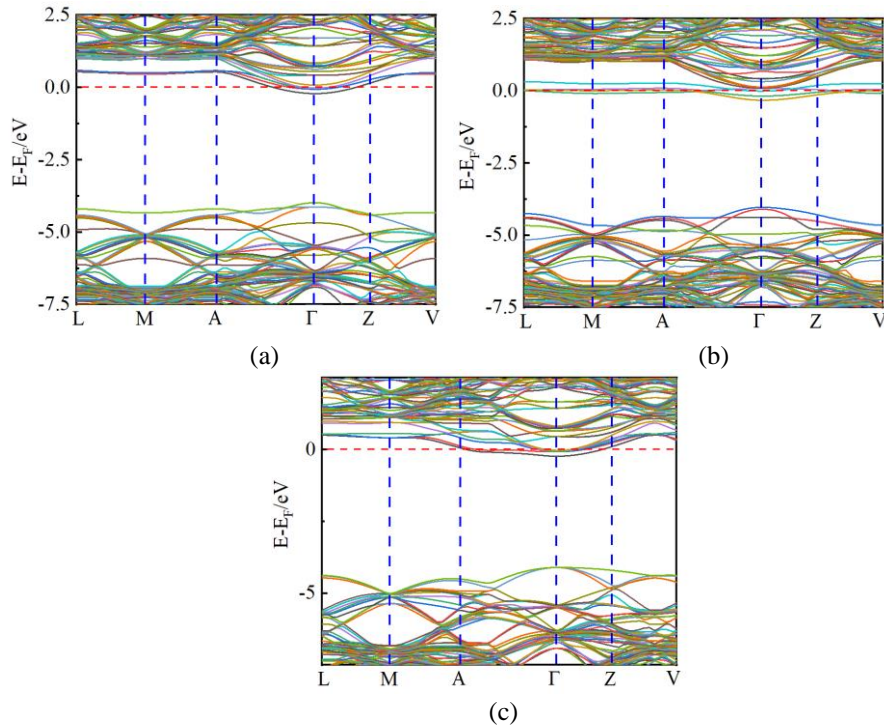

(a)　　(b)　　(c)

Fig. 5. Band structures of doped diamond with Be-N_3 (a), Be-O_2 (b), and Be-S_2(c)

4   Conclusions

In conclusion, Be-related co-doping is expected to achieve N-type doping in diamond. Co-doped N, O, and S atoms not only reduce the formation energy, but are also a key factor in achieving n-type doping. Be-N, Be-O, and Be-S co-doped systems are expected to achieve diamond n-type doping, and the performance of Be-N co-doping is the best overall. We systematically calculated the formation energy, ionization energy, band structure, and DOS of various doped structures. These calculation results all prove that BeN3 has outstanding performance among Be-related co-doping structures and is expected to achieve high concentration and shallow doping of n-type diamond. Our calculation results need to be further verified by experiments.

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