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Electronic structure and impurity states of S-doped cBN: A first-principle study

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ABSTRACT

The electronic structure and impurity states of S-doped *c*BN were investigated by first-principle approaches. Our calculation shows that S substituted for an N atom creates shallow donor levels merged to the states at the conduction band edge, S substituted for a B atom creates deep donor levels within the band gap, both forming

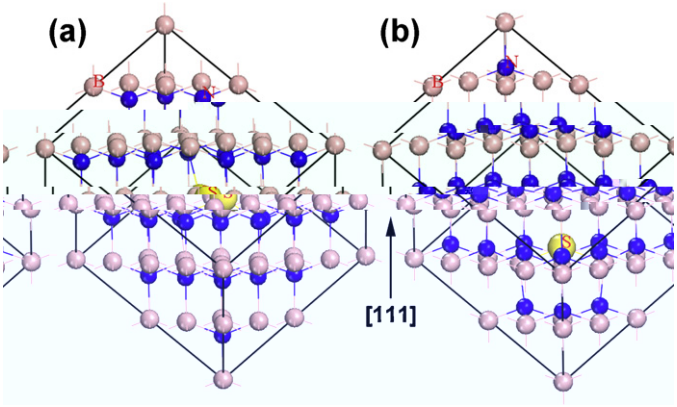

Fig. 1. 64-Atom supercell structure (a) S substitution at the B site; (b) S substitution at the N site. Pink ball: B; blue ball: N; yellow ball: S.

sulfur atom substitution at the center or near center of each supercell, yielding an effective impurity concentration of 3.13%, 1.56%, 1.04% and 0.78%, respectively. All atomic coordinates were relaxed and the structure optimization was performed until the energy change of per atom was less than 1.0×10^{-5} eV, the Hellmann–Feynman forces on atoms were less than 0.03 eV/Å, and the maximum displacement of per atom was 1.0×10^{-3} Å. Note that the scissor operation of 1.9 eV [25,26], a linear shift of the calculated band structure, has been used to correct the theoretical bandgap compared with the widely admitted experimental value, due to the well-known underestimation to all of the LDA calculations in which the correlation energy of excited electrons is ignored. Another theoretical investigation using the general gradient approximation (GGA) was also performed to check the accuracy, and the lattice parameters and band gap of pure cBN agree well with each other (shown in Table 1) and previous experimental results [27].

3. Results and discussion

Supercell structure of sulfur impurity substitutions at a B atom and an N atom (taking a 64-atom supercell as an example) are shown in Fig. 1. Total energy values of different supercell sizes are shown in Fig. 2a, and we can see that the total energy of S substitution at the B site is less than that of S substitution at the N site, which means that S substituting at the B site is easier and structural stable. This calculation result is consistent with our previous experiment [28]. As shown in Fig. 2b, for a cBN film prepared by PECVD with the introduction of H_2S into the deposition system, the increase of S second ion intensity measured from the depth profile second ions mass spectroscopy (SIMS) of the S-doped cBN was accompanied with a decrease of B second ion intensity, suggesting that S is mainly substituted for B atom. Fig. 2a also shows that the total energy difference between S atom substitution at the N site and at the B site is independent on the supercell sizes, remaining about 190 eV. This mainly results from that the difference of formation energy between S substitution at the B and N site with same cell size is a constant where influence of supercell size is minimized.

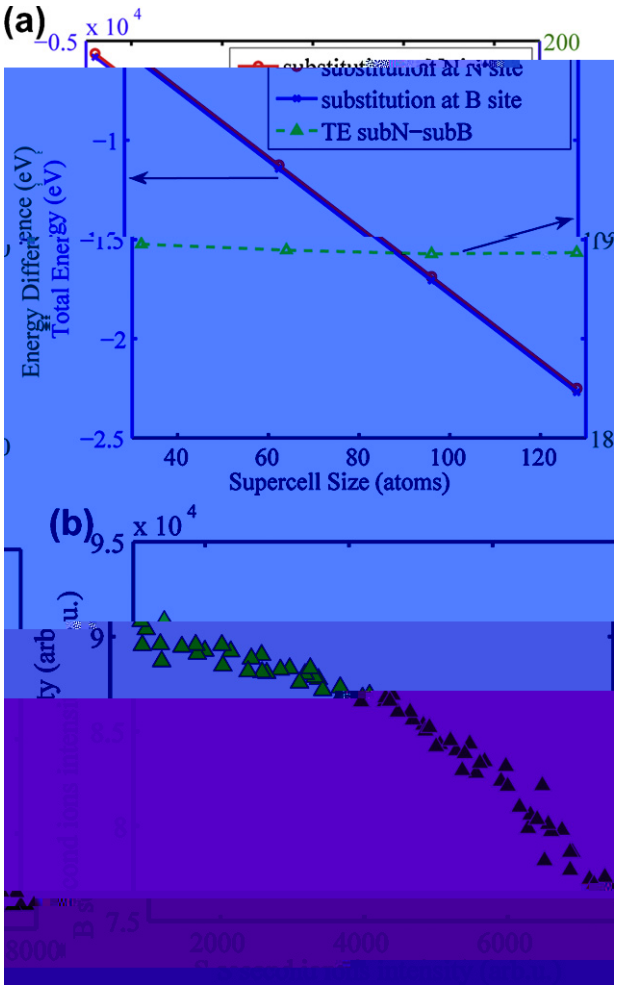

Fig. 2. (a) Total energy of varying cBN supercell size and energy difference between S substitution at the B and N site. The total energy of S substitution at the B site is about 190 eV less than that of S substitution at the N site with the same supercell size. (b) Second ions intensity of S and B in an S-doped cBN film measured by depth profile SIMS. S-doped cBN films were prepared by PECVD.

The calculation of energy band structure of ideal intrinsic cBN indicates that pure cBN is indirect bandgap semiconductor material with a minimum bandgap of ~6.29 eV between G and X in the reciprocal space (shown in the inset of Fig. 3a and Table 1), consistent with previous results [27,29]. The energy band of S-doped cBN is much complicated, mainly due to impurity atoms inducing energy levels of hybrid orbitals when forming S—B bonds or S—N bonds. Total electron density of states (DOS) for cBN with different S-doping levels presented in Fig. 3 indicates the details of band structure variation with sulfur concentration. We note that the bandgap decreases as the impurity concentration increases. The calculated bandgap is 5.41, 5.35, 5.25 and 4.95 eV for S substitution at the N site with doping concentration of 0.78%, 1.04%, 1.56% and 3.13%, respectively. For S substitution at the B site, the calculated bandgap is 5.62, 5.55, 5.03 and 4.63 eV (shown in the inset

Table 1
Geometry optimized structural parameters and band gap of pure cBN comparing with GGA approach and experimental results.

	This work		Literature [27]
	LDA/CA-PZ	GGA/PBE	
a (Å)	3.588	3.638	3.615
B—N bond length (Å)	1.554	1.575	1.570
Band gap (eV) (scissor = 1.9 eV)	4.39 + 1.9 = 6.29	4.44 + 1.9 = 6.34	6.1–6.4

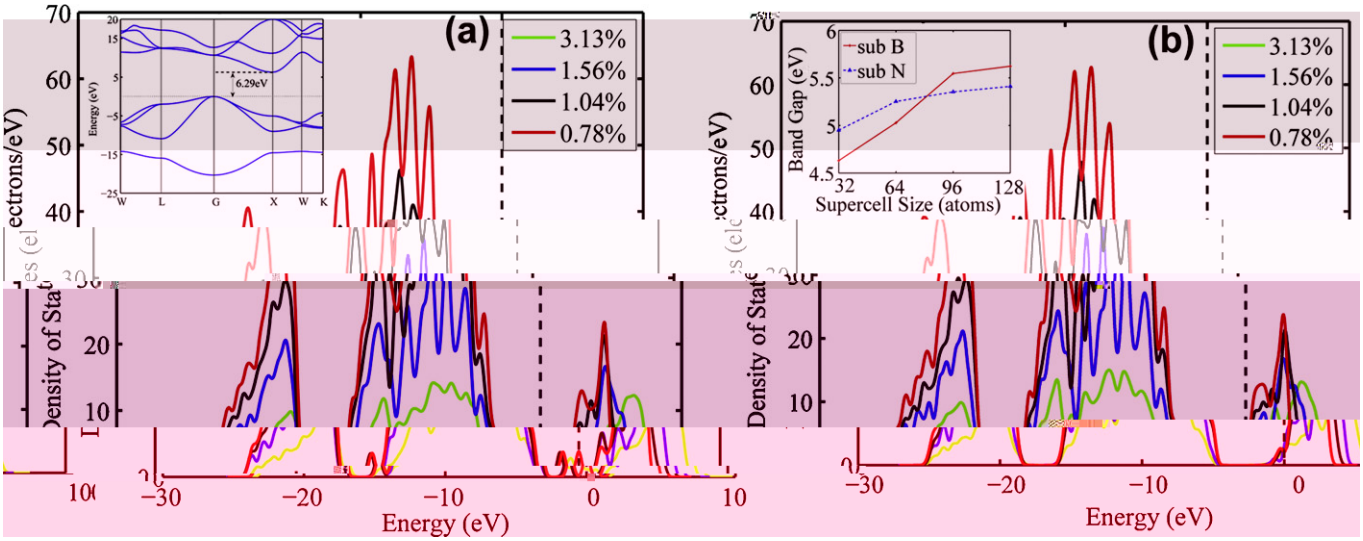

Fig. 3. Density of states of different S-doping level cBN. (a) S substitution at the B site (inset is the calculated energy band scheme of pure cBN). (b) S substitution at the N site (inset is the relationship between band gap and supercell size).

of Fig. 3b). As analyzed in the following section, this might result from that one of the S 3p orbitals which is near the conduction band hybridizes with B 2p orbital.

To further investigate contributions of different atom species to the energy level, partial density of states (PDOS) of S-doped cBN is displayed in Fig. 4. When S substituted at the B site, S 3s orbital overlap with its neighboring nitrogen 2s and 2p orbital, forming one peak at the bottom of upper valance band (about −14.7 eV), and two of the S 3p orbitals hybridize with N 2p orbital, resulting in deep energy levels within the band gap (about −1.3 eV and 0 eV); another S 3p orbital hybridizes with its neighboring N 2p orbital, forming peaks at the conduction band (shown in Fig. 4a and c). While for S substitutes at the N site, S 3s orbital hybridizes with its neighboring B 2s and 2p orbital forming peak at the top of lower valance band; two of the S 3p orbitals forming bond with B 2p, forming peaks at the bottom of upper valance band, and another S 3p orbital hybridizes with its neighboring B 2p orbitals, forming peaks at the conduction band (shown in Fig. 4b and d). The PDOS analysis shows that the substitutional S atom induces certain impurity states within the bandgap and near band edge of pure cBN bulk, resulting in the bandgap reduction from 6.3 eV of pure cBN to 4.6 eV and 5.0 eV (3.13% impurity concentration) of S doped at the

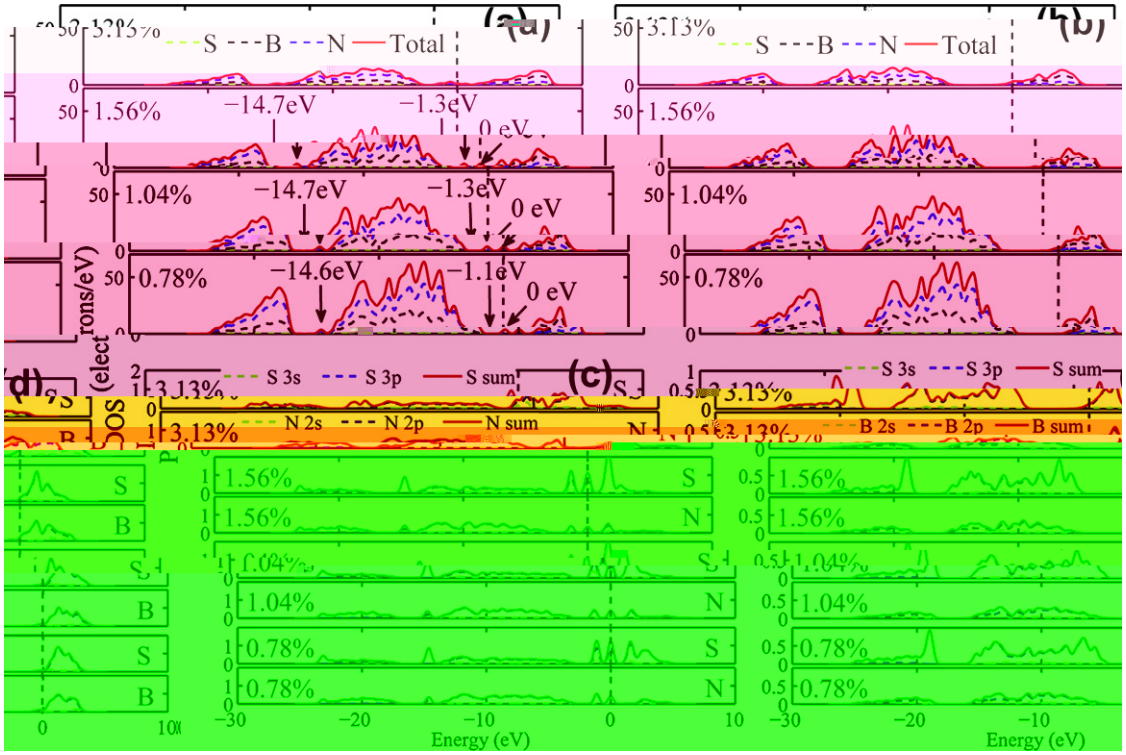

Fig. 4. Partial density of states of S-doped cBN with different doping levels (a) contributions of different elements where S substitutes at the B site, (b) contributions of different elements where S substitution at the N site, (c) PDOS of S atom and its neighboring N atom where S substitutes at the B site, and (d) PDOS of S atom and its neighboring B atom where S substitutes at the N site.

B and N site, respectively. Particularly, when S substitutes at the B site with a doping level of 3.13%, the PDOS of S atom shows that electron states have almost occupied within the whole bandgap, which is different from the PDOS of the other three doping levels. In the three less S-content levels, S induced discrete energy levels in the bandgap. The reason might be that 3.13% S-doping level is high that the doped cBN crystal has become degenerate. As a result, the S atom substitution at the B site induces deep impurity level, while the S atom substitution at the N site induces shallow level within the band gap. The greater negative total energy in the case of S substitution for B (S → B) than for N (S → N) shown in Fig. 2 suggests that bond energy of S(S → B)—N is stronger and more stable than that of S(S → N)—B. This can be explained by the number of valance electrons of an S atom. That is, S(S → N) and S(S → B) have one or three more valance electrons than the original N or B atoms in the unperturbed lattice, respectively. On the other hand, electron state of S(S → B) is less localized than that of S(S → N) due to closer electron affinity between S and N than the case between S and B bonds. It means that higher transition probability for carriers is expected