Comment on “Mechanisms of Postsynthesis Doping of Boron Nitride Nanostructures with Carbon from First-Principles Simulations”

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Comment on "Mechanisms of Postsynthesis Doping of Boron Nitride Nanostructures with Carbon from First-Principles Simulations"

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In Ref. [1], Berseneva *et al.* calculated the formation energies of C substitution at B or N site ($C_{B/N}^{q}$) in BN sheet with charge state q from -3 to +2. They proposed that the defect formation energies of $C_{B/N}^{q}$ can be reduced by charging the system during irradiation. Although the proposal is intriguing, it is difficult to understand why simple substitutional defects such as C_B or C_N can sustain charge state all the way from q=-3 to q=+2, because the valence difference between C and B or N is 1 so the number of electrons one can add or remove from the defect levels should be limited [2]. In the following, we will show that the calculated formation energies of some of the charged defects and the corresponding defect transition energy levels (Figs. 2, 3 in Ref. [1]) are incorrect. We also point out that one cannot lower the formation energy of donor such as C_B by making it positively charged, as suggested in Ref. [1].

For the case of C_B (Fig. 1a) in neutral charge state, because C is more electronegative than B, there is a defect level pulled down from the conduction band with C p_z component and it is occupied (unoccupied) in spin-up (spin-down) channel, agreeing with previous calculations [3]. When an extra electron is added to the defect level (q=-1, Fig. 1b), the defect levels shift up in energy due to Coulomb repulsion between the occupied electrons. The nearly-free-electron (NFE) state near the conduction band minimum (CBM) [4] moves down in energy rapidly when extra electrons are added [5]. The net effect is that the NFE becomes partially occupied. Further addition of electron to the defect level cannot be realized because it is now above the NFE state. When an electron is removed from the spin-up defect level (q=+1, Fig. 1c), the defect levels move down in energy and the system becomes non-spin-polarized. No more electrons can be further removed from the defect level because there are no more electrons left at the defect level. Our analysis above clearly indicates that C_B defect in BN sheet can only realize (-1, 0, +1] states, so the formation energies of C_B in its -3, -2, and +2 charge states and corresponding transition levels shown in Figs. 2a, 3a of Ref. [1] are incorrect. Similar arguments can be applied to C_N defect. From Figs. 1d-1f, we see that C_N defect can only realize -1, 0, and +1 states. Therefore, the formation energies of C_N in its -3, -2, and +2 charge states and the corresponding defect transition levels shown in Figs. 2b, 3b of Ref. [1] are incorrect. Our HSE calculations also support our conclusion got from PBE calculations. The same error also exists in the formation energies of $4C_{3B1N}^{-3}$ and $4C_{3N1B}^{-3}$ shown in Figs. 2c, 2d in Ref. [1] because only charge states from +2 to -2 can be realized.

We also want to point out that in general one cannot lower the defect formation energy by controlling the charge state of the defect itself. For examples, C_B can have low formation energy when it has +1 charged state and the Fermi energy is close to VBM. However, when C_B is in +1

charged state, the donated electron and the required charge neutrality condition will shift the Fermi energy more close to CBM than VBM, where C_B^{+1} actually has high formation energy.

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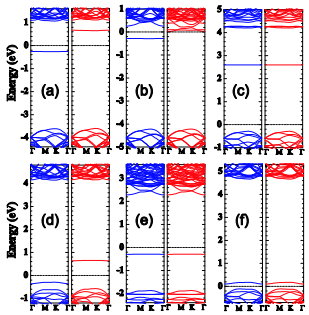

Figure 1. (a)-(c): The PBE band structures of C_B defect in its neutral, -1, and +1 charged state, respectively. (d)-(f) are the same as (a)-(c) but for C_N defect. Fermi level is set to zero.