Tuning the electronic and magnetic properties in zigzag boron nitride nanoribbons with carbon dopants

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Abstract

We report a first-principles investigation on the tuning effects of carbon dopants on the electronic structures and magnetic properties of zigzag boron nitride nanoribbons (ZBNNRs). In particular, 10-ZBNNR is considered and a supercell with five unit cells is adopted in the calculations. When the supercell is doped by one carbon (C) atom, the dopant tends to substitute the edge atom resulting in a 0.625μB magnetic moment on the dopant and the system becomes a magnetic semiconductor. By changing the dopant position, namely, from the edge to the ribbon center, the nanoribbon transforms from a magnetic semiconductor into a metal. If the edges of the supercell are doped by two C atoms, the nanoribbons become a nonmagnetic semiconductor. With the increase of the dopant concentration, the conductivity of the ZBNNRs can be greatly improved. Especially, with careful design of the dopant distribution, half-metallic ZBNNRs can be achieved.

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1. Introduction

In the past decade, boron nitride nanotubes (BNNTs) have received great attention [11], due to their high thermal and chemical stabilities, and the great potential for applications as protective shields of some nanomaterials, nanostructured composite materials, and nanoscale electronic devices, even at high temperatures and/or in hazardous environments [2,3]. Extensive studies on BNNTs have also stimulated researchers’ great interest in single-layer hexagonal BN (h-BN) nanosheets and, especially, BN nanoribbons (BNNRs), a structural analogy of graphene nanoribbons (GNRs).

Due to the large ionicity of B and N, BNNRs exhibit novel properties different from GNRs, leading to new potential applications for deep UV optoelectronic devices [4,5]. BNNRs are found to be strong and stable quasi-one-dimensional structure. Unlike GNRs, the H-terminated BNNRs are intrinsically insulators or wide-band gap semiconductors. First principles calculations indicate that the band gap of H-terminated BNNRs are dependent not only on the edge shapes (zigzag and armchair) but also on the ribbon width. For zigzag BNNRs, the band gap is indirect and decreases monotonically with increasing ribbon width due to the enhanced charge transfer from the B edge to the N edge, while gap oscillation is found for armchair BNNRs [6–8]. However, the wide band gap of BN nanomaterials is a substantial obstacle for their application in electronics. In significant efforts to reduce the band gap, various approaches have been proposed to modulate BNNRs, such as electric field application [6], edge modification [9–14], strain [15], defect introduction [16,17], hydrogenation [18], impurity or molecular doping [19,20].

In particular, inspired by making p-type and n-type semiconducting graphene by substituting C atoms with B and N atoms, respectively, many researchers considered C atom as the most suitable impurity in BNNRs doping. Experimentally, it has been found that B and N atoms in BN nanostructures can be substituted by C atoms under electron-beam-induced doping [21,22]. The experiment results showed that BN nanosheets, BNNRs and BNNRs transform from insulators to conductors through intentional C-doping, and the preferential doping site is found to occur at BNNR edges [23,24]. Theoretically, Beheshtian et al. found that doping BNNRs by a zigzag line of carbon atoms decreases the band gap, while the electric polarization of the doped BNNRs depends on the types of atoms (B or N) that surround the dopants [25]. Even in the absence of an external electric field, carbon chain-doped zigzag BNNRs (ZBNNRs) with one H-saturated boron edge and one bare carbon edge exhibit half-semiconducting → half-metallic → metallic electronic behavior transitions as the number of zigzag carbon chains replacing the zigzag boron–nitrogen chains gradually increase [26]. More interestingly, B, C and N can be atomically mixed together to form BCN-hybrid systems. First-principles calculations have indicated that armchair BCN-hybrid nanoribbons show half-
metallicity and d^0 magnetism [27,28]. Additionally, it has been revealed that single C-substitution at either single boron or nitrogen atom site in BNNRs could induce spontaneous magnetization [29].

In this work, we report spin-polarized density functional calculations for the ZBNNRs which are randomly doped by low-density carbon atoms and passivated by hydrogen atoms at the edges. We studied different possible positions of C-doping and found that the local magnetic moment induced by single C-doping in a supercell containing five unit cells is dependent on the position, and reaches the maximum of 0.625\(\mu_B\) when the C dopant lies at the edges. This finding is distinctly different from Tang et al.'s investigations, which show that the magnetic moments induced by carbon doping keep at about 1.0\(\mu_B\), irrespective of the doping site and density [30]. In addition, for the cases with two or more C dopants in the supercell, magnetism is mostly not found in the doped ZBNNRs, but magnetic semiconductors, half metals, and magnetic metals could be obtained at certain dopant location. Consequently, it is highly feasible that these intriguing properties can be achieved in the unitary BN-based nanomaterials, which is advantageous for the design of functional devices.

The rest of this paper is organized as follows: in Section 2 we give a brief description of the structures studied in this work and the computational method, while in Section 3 the main results are presented and discussed. Finally in Section 4 we draw out conclusions.

2. Computational details

The calculations are performed by using the SIESTA code which employs norm-conserving pseudopotentials and linear combinations of atomic orbitals as basis sets [31]. The wave function is expanded with a double zeta polarized (DZP) basis set and the exchange–correlation potential is treated at the level of generalized gradient approximation (GGA), with the form of Perdew–Burke–Ernzerhof (PBE) [32]. The fineness of real space grid is determined by an equivalent plane wave cutoff 200 Ryd. In this work, we take 10-ZBNNR (10 zigzag boron nitride chains along x axes, the width direction of ribbon.) as an example and the supercell of the pristine ZBNNR consists of five unit cells with the length of 12.3 Å (see Fig. 1). The lattice vectors along the x and y axis are set to be 35.0 Å and 15.0 Å, respectively, which include a vacuum big enough to avoid interactions from the adjacent neighbors. The Brillouin zone is sampled by a 1 \times 1 \times 1 k-point grid. All the structures are fully relaxed until the force tolerance of 0.04 eV/Å is reached. All the optimized geometry structures of 10-ZBNNR are terminated by hydrogen atoms.

3. Results and discussion

The ground state of the pristine 10-ZBNNR in our calculations is a nonmagnetic insulator with a wide band gap of 4.2 eV, which agrees with the previous DFT calculations [30]. The top valence band is mainly from N atoms close to the N edge, while the bottom conduction band is mainly from the B atoms close to the B edge. The edge state from N atoms is more extensive than that from B atoms. In the following, at first, the influence of a single carbon doping, with one B or N atom substituted by a C atom, on structural and electronic properties of 10-ZBNNR was investigated. For the sake of convenience, the carbon atoms replacing B or N atoms are labeled as C_a or C_b, respectively.

In order to reveal the effect of doping sites on the electronic magnetic properties of ZBNNRs, various sites of B atoms along the width direction of ribbon were chosen as the C-doping sites (various sites of N atoms are not shown here), labeled as C_a, C_b, . . . , C_j (see in Fig. 1). Our calculations show that the fully relaxed equilibrium geometries of C-doping are similar to that of the pristine ZBNNR. The main perturbation in geometry arises from the shortened N–C bond length of 1.39 Å or the elongated B–C bond length of 1.51 Å, as compared with the B–N bond length of 1.43 Å. The carbon-induced perturbation is of a local nature and only has slight effect on adjacent rings. In the case of C_a, to evaluate the relative stability of C-doping at different doping sites, the total energy difference \(\Delta E\) is estimated by \(\Delta E(C_j) = E(C_j) - E(C_a)\), \(x = a, b, c, d, e\) and is shown in Table 1. It is seen that \(\Delta E\) decreases from 1.59 eV at C_j to 0 at C_a as the C-doping site approaches the B edge. Obviously, C-substitution preferentially occurs at the edge, which agrees well with both the experimental and previous theoretical results [23,24,30]. Such C-doping characteristics arises from the fact that the edge atoms possess lower potential and these sites are more vulnerable to the electron beam irradiation.

The electronic band structures with dopants at different positions are shown in Fig. 2. From C_a to C_j, the spin polarization of energy band happens to be quite different. Meanwhile, the upshift of the Fermi energy of the system relative to the pristine ZBNNR is observed due to C_a acting as a n-type doping. Moreover, two flat spin-up and spin-down bands emerge within the wide gap of the pristine ZBNNR, which is induced by the carbon dopant. When the dopant is close to the edge, the band structures are spin polarized (see Fig. 2(a, b, e, f, g, i)). with the spin-up channel near the Fermi level fully occupied while the spin-down left empty, with a net magnetic moment on the C atom observed. Take the C_a doping case as an example, 0.625\(\mu_B\) is found on the C atom. According to Mulliken population analysis, its two adjacent B edge atoms possess 0.105\(\mu_B\), respectively. The C_a doped ZBNNR is a magnetic semiconductor, for which the band gaps of the spin-up and spin-down channels are 1.59 and 3.87 eV, respectively. However, as the dopant moves away from the edge, the spin polarization is gradually suppressed. In the case of C_e, C_d, and C_b, the spin-up and spin-down band structures of the doped ZBNNR are degenerate with vanishing magnetic moment. The unpolarized dispersion-less bands induced by carbon dopant cross the Fermi energy, which contributes a very sharp peak in the density of states (DOS) and will lead to structural and magnetic instability (Stoner instability). Thus the C dopant tends to segregate from the center to the edge and simultaneously, get the spin degeneracy broken. This is confirmed by the much lower total energy (see Table 1) and spin polarized band structure (see Fig. 2) with the dopant at the edges.

From the above analysis, we find that non-magnetic impurity may induce finite magnetic moments in ZBNNRs. However, can

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the local magnetic moments result in collective magnetism? The question involves long-range magnetic coupling and is a crucial issue for applications. Therefore, we further explored the magnetic interactions between the C-induced magnetic moments in ZBNNRs. When two C impurities are introduced into the original supercell of the ZBNNR, there are many possible configurations corresponding to different distances between the substituted atoms. Wei et al. found that there is a higher C content at the edges and within some flaked internal areas in the BN nanosheet via electron-beam-induced C-doping [24]. Thus, they are most probably located at the edges, or form a dimer (substitution of a pair of carbon atoms at the neighboring B and N sites) under the condition of low-density C-doping.

When two dopants initially substitute a BN pair in the same hexagonal ring of the ZBNNR (The distance between two C atoms is the shortest, shown in Fig. 3), the local magnetic moment induced by each C atom is completely suppressed as a result of the formation of a C dimer (C_{di}). The whole system is a nonmagnetic semiconductor with a band gap of 3.3 eV, which can be seen from the band structure shown in Fig. 3(a). Apart from reducing the band gap, two dopants produces new dispersionless and degenerate bands in the gap. Red square and green circle represent C–C bonding state and C–C antibonding state, respectively. To explore the C-doping induced localized state, the wave functions at the \Gamma point of selected bands are depicted in Fig. 3(b and c). A C–C covalent bond is formed from the overlap between the nonbonding states of the dopant atoms, which is responsible for the nonmagnetic state of C_{di}.

Next, we gradually increased the initial distance between two C impurities along the B edge (two C atoms replace the two adjacent B atoms at the edge, which is denoted by C_{aa}) and performed the structural relaxation. Although the dimerization does not occur when two C dopants are initially placed into two different BN hexagonal rings, the local magnetic moment on C_{aa} is also entirely quenched. The main reason may be that the C_{aa}’s nonbonding state is far more extended due to the influence from edge states. When the two C atoms are at adjacent B edges for C_{aa} case, the wave functions of C atoms overlap to the largest extent. The two nonbonding electrons share with each other and form one quasi covalent bond. Therefore, the system is nonmagnetic semiconductor (Fig. 4(a and c)).

When two C atoms are not at adjacent edge atoms (C_{ah}), the distance between them is so large that the quasi covalent bond does not occur. According to the calculation results, each C_{ah} has a
magnetic moment of 0.625μB, but the antiferromagnetic state (AFM) is most stable for this system. The doped ZBNNR presents nonmagnetic semiconducting behavior with a gap of 1.13 eV (Fig. 4(b and d)). This magnetic interaction can be conveniently illustrated by the nearest-neighbor Heisenberg model (shown in Fig. 5). Every C atom has one unsaturated valence electron and the corresponding impurity state is half filled, so virtual hopping is allowed in the AFM arrangement but not allowed in the ferromagnetic (FM) configuration, resulting in a lower energy AFM state. Nevertheless, the nearest-neighbor magnetic coupling is a function of dopant separation. When the separation is so long that the interaction between the magnetic moments is very weak, the AFM and FM configurations of the doped ZBNNR will become degenerate.

On the basis of the above results, after doping two carbon atoms into the original supercell of ZBNR, the total magnetic moments of the doped ZBNNRs are shown to be zero. However, Berseneva et al. showed that triangular carbon islands embedded into BN sheets possess finite magnetic moments [23,33], which inspired us to suppose that the total magnetic moment would not be zero for the system with doping one more carbon atom. Two different configurations of three carbon atoms were just considered. The dopants are at adjacent edge sites (C<sub>aaa</sub>) and at nearest-neighbor sites (C<sub>dd</sub>), respectively. The results are described in Table 2. Surprisingly, the local magnetic moment induced by each C impurity is preserved, which indicates that there is neither the covalent bonding nor quasi covalent bonding between nonbonding states of C dopants. In addition, local magnetic moments are in AFM arrangement due to magnetic interaction, so the total magnetic moment is not zero. However, its magnitude varies with the different dopant distribution as well as the band gap of the doped ZBNNR.

When carbon substitutions are asymmetric at B and N edge sites (one at B edge and the others at N edge), new narrow bands appear and cross the Fermi energy, which arise from the localized states induced by dopants. We performed calculations for two different spin orderings similar to GNRs: (i) ferromagnetic, with spins on the three carbon atoms parallel and (ii) antiferromagnetic, with spins of the carbon atoms on different edges antiparallel. The results show that the antiferromagnetically coupled state has the lower energy. Meanwhile, the magnetic moment on each dopant and electronic structures are dependent on how these dopants are distributed. In most cases, the doped ZBNNRs are metallic, however, when one carbon atom is located at the B edge of the first unitcell, and the other two carbon atoms are located at the N edge of the third and the fifth unitcells, half-metallicity can be achieved (see Fig. 6). The magnetic moment of carbon atom doped at B edge site is 0.485μB, and the magnetic moment on the N edge is 0.596μB. Furthermore, the local magnetic moments of the carbon atoms at the same edge are coupled ferromagnetically while antiferromagnetically for those at different edges.

4. Conclusion

In summary, we have systematically studied the effects of C-doping in zigzag boron nitride nanoribbons by first-principles density functional theory calculations. We found that substitution of carbon intends to occur at edge sites due to lower site energy. One dopant at the B edge site possesses the magnetic moment of 0.625μB, which arises from the polarized nonbonding state of carbon by localized edge state. With the edge state decaying inward, the induced magnetic moment at the middle site decreases to zero. Furthermore, the new dispersionless band corresponding to the localized state arise at the Fermi level. With two carbon atoms doped in the ZBNNR (at edge sites or at the nearest neighbor sites), the total magnetic moment is zero. With another more dopant, the total magnetic moment is dependent on the locations of the carbon atoms. The system can be either a magnetic semiconductor or a metal. Especially, with careful control over the distribution of the carbon dopants, half-metallicity can be achieved. This opens new possibility for its application in spintronic devices.

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### Table 2

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### References
