ORIGINAL ARTICLE

Electronic and transport properties of boron and nitrogen doped graphene nanoribbons: an ab initio approach

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Abstract Graphene nanoribbons (GNRs) are expected to display extraordinary properties in the form of nanostructures. The effect of boron and nitrogen substitutional doping at four successive positions on electronic and transport properties of zigzag graphene nanoribbons (ZGNRs) is studied using spin-unpolarized density functional theory. It has been observed that the electronic structures of the doped ZGNRs are different from those of pristine ZGNRs. We have also calculated the transformation energy in the form of total energy. The substitutional boron atom at the nanoribbons edges suppresses the energy band near Fermi level by changing properties of material from metallic to semi-metallic in ZGNRs which can be explained as a consequence of the edge polarization effects. At all doping positions, N-doped ZGNRs are n-type while B-doped ZGNRs are p-type semiconductors. These substitutionally B- and N-doped impurities act as scattering centers for transport in GNRs. Due to unusual properties of these nanomaterials, they can be used in carbon-based nanoelectronics devices.

Keywords Graphene nanoribbons · Density functional theory · Boron · Nitrogen · Doping

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Introduction

The high electron mobility and long coherence length make graphene a subject of great interest for nanoscale electronics applications. However, the main problem in the development of graphene based field effect transistors is the inability to electro-statically confine electrons in graphene. This is because a single layer of graphite remains metallic even at the charge neutrality point. Due to that problem, a way to open a gap in electronic structure of graphene has to be found. One of the solutions of such problem is to pattern the graphene sheet into nanoribbons. Carbon nanostructures are available in a variety of forms such as fullerenes (Kroto et al. 1985), carbon nanotubes (CNTs) (Iijima 1991), and 2D graphene (Novoselov et al. 2004). The two-dimensional graphene has attracted much interest due to its peculiar electronic as well as transport properties described by massless Dirac equation (Castro Neto et al. 2009; Geim and Novoselov 2007). A good number of literature is available in both experimental (Geim and Novoselov 2007; Lee et al. 2008) and theoretical (Castro Neto et al. 2009; Fujita et al. 1996) studies to understand the electronic (Castro Neto et al. 2009), transport (Novoselov et al. 2005), and optical properties (Dresselhaus et al. 2010) of graphene. Narrow graphene ribbons (GNR) are fabricated (Han et al. 2007) and predicted to have a major impact on their electronic transport properties (Son et al. 2006). The electronic properties of GNRs are mainly dependent on the width and atomic geometry of their edge by opening an energy gap, namely, zigzag or armchair (Castro Neto et al. 2009). In view of the interest in the research of edge states in the electronic structure of zigzag graphene nanoribbons (ZGNRs), they exhibit promising potential applications in spintronics (Son et al. 2006). The electronic properties of ZGNRs can be

effectively functionalized via vacancies (Chauhan et al. 2011a, b), topological defects (Cortijo and Vozmediano 2007), adsorption (Choi and Jhi 2008), doping (Chauhan et al. 2011a, b), chemical functionalization (Cantele et al. 2009; Cervantes-Sodi et al. 2008), and molecular junctions (Wang et al. 2009). There are various defects in GNRs which mainly include the Stone–Wales defect (Park et al. 2008), adatoms (Yan et al. 2009), vacancies (Topsakal et al. 2008), substitution (Peres 2007), and disorder (Long et al. 2008). Theoretical studies based on spin-polarization calculations suggest that pristine ZGNRs are semiconductors, with a band gap opening as a result of the presence of edge states, which are ferromagnetically ordered but anti-ferromagnetically coupled to each other (Son et al. 2006). The electronic transport properties of carbon nanostructures can be controlled through substitutional doping (Jianwei et al. 2007). Nitrogen-doped carbon nanotubes (CNTs) have great possibilities for electronic applications by manipulating the electronic properties of semiconducting single wall carbon nanotubes (SWCNTs) (Ehli et al. 2009). Doping GNRs with boron atoms can also lead to the metal to semiconductor transition and break the polarized transport degeneracy (Martins and Miwa 2007). The conductance of doped GNRs strongly depends on the ratio and the position of the impurity (Chauhan et al. 2011a, b). However, the influence of different doping sites on the electronic properties of GNRs with zigzag edges received little attention (Zheng and Duley 2008; Yu et al. 2008). Importantly, in view of chemically synthesized and lithographically patterned process of GNRs fabrication, it seems impossible to avoid the presence of other impurities, especially for the nitrogen substitutional doping, in the atomic structure of graphene nanostructure (Li et al. 2008). The nanotube can transform from intrinsic semiconductor to n-type or p-type semiconductor (Yu et al. 2007). Likewise, when a ZGNR is doped with nitrogen or boron atoms, its electronic properties are also affected strongly (Martins and Miwa 2007; Dutta and Pati 2008; Huang et al. 2007; Yan et al. 2007; Miwa et al. 2008). The doping site also influences the electronic properties of ZGNRs doped with N atom (Zheng and Duley 2008). ZGNRs have a very large density of states at the Fermi level, which is attributed to the edge-localized states having nonbonding character (Wakabayashi et al. 1999; Brey and Fertig 2006). Due to the unpaired $\pi/\pi*$ edge electrons, ZGNRs exhibit ferromagnetic susceptibility (Son et al. 2006; Wakabayashi et al. 1999) structures. Graphene nanoribbons are nanometer-sized strips of single-layer graphene and have been the focus of extensive experimental and theoretical efforts (Wakabayashi et al. 1999). Due to their structural resemblance to CNTs and quantum confinement effects, GNRs are expected to have electronic properties similar to the CNTs that can be unwrapped into GNRs (Barone et al.

2006). The electronic properties of nanoribbons can be determined by the width and atomic geometry along the edge namely, ZGNRs or AGNRs (Son et al. 2006; Brey and Fertig 2006). It is well known that nitrogen and boron atoms are typical substitutional dopants in carbon materials and they can inject electrons or holes, thus change their electronic and transport (Lee et al. 2005) properties. Motivated by the recent experimental and theoretical progress in this area, we perform the spin-unpolarization density functional theory (DFT) calculation to investigate the effect of isolated substitutional nitrogen and boron doping at various sites on the electronic band structures, density of states and transport properties of ZGNRs with hydrogen-terminated edges.
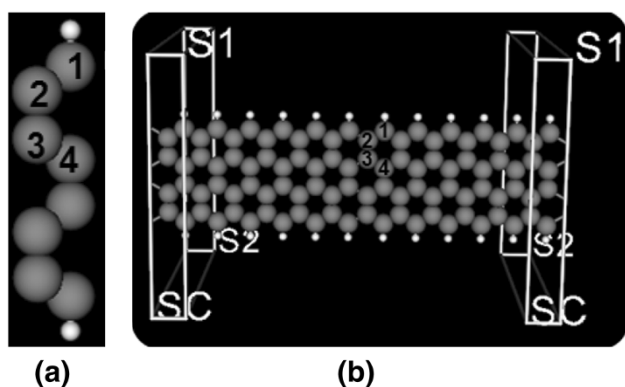
Methods

The first-principles electronic and transport calculations are performed using an ab initio code package, Atomistix ToolKit 10.08.0 (ATK) (Chauhan et al. 2013), which is based on real-space, non-equilibrium Green's function (NEGF) formalism and the spin unpolarized density-functional theory (DFT). The calculations of the complete system can be obtained from two independent calculations of both electrode regions and a two probe calculations of the central scattering region. The electrode calculations are performed under periodical boundary conditions, with the unit cell being six atomic layers along the ribbon axis, and the sampling of Brillouin zone integration is performed using Monkhorst-pack parameters with a regular k-point grid $1 \times 1 \times 100$ for electronic relaxation. Energy cut off of 2500 Rydberg and double zeta polarization basis orbitals were used for many atoms in a unit cell of ZGNRs of various widths. The electrodes are kept at 0 V. Self-consistent calculations are performed with a mixing rate set to be 0.1, and the mesh cutoff of carbon atom is 150 Ry to achieve a balance between calculation efficiency and accuracy. The approximation for the exchange–correlation functional is the spin-unpolarized local density approximation (LDA). The C–C and C–H bond lengths are set to be 1.42 and 1.1 Å, and these values had been already tested (Ordejón 1996).

Results and discussion

To fabricate a device with a different material requires understanding all the factors that influence its electronic and transport properties. The geometry and the presence of various forms of chemical modifications are crucial for graphene nanoribbons. The geometry is defined by length, width, and edge chirality, whereas chemical modifications

can be caused by different edge terminations and by substitutional atoms in the ribbons' body. As shown in Fig. 1a, 8-ZGNRs per seven units is chosen as a model system to study the electronic structures of N-doped and B-doped ZGNRs with four doping sites, and the corresponding total energies are calculated to determine the most energy-favorable site. In case of B substitutional dopant, the corresponding energy differences are −0.18, 0.02, and −0.06 eV, respectively (Table 1). The site 3 for B doping is the most energetically favorable site. For N doping, the calculated substitution energy of site 1 is less than that of site 2 (by 0.47 eV), site 3 (by 0.23 eV), and site 4 (by 0.32 eV) as in Table 2. This clearly indicates that an energetic preference of N is at the edge of 8-ZGNRs for site 1.

The electronic band structures for B-doped ZGNRs are shown in Fig. 2a–e and for N-doped ZGNRs shown in Fig. 3a–e. Calculations show that the pristine 8-ZGNRs is a metallic with zero band gaps in Fig. 2e. It is observed that the electronic structure is significantly modified and transformed from metallic to semiconducting by doping. Near the Fermi level, there are two energy levels whose corresponding molecular orbitals are the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). The Fermi level is shifted upward due to the extra π electrons from the N atom as in Table 2 and is shifted downward due to vacancy of electron from B atom as in Table 1. Near the Fermi level, the conduction band structure is perturbed by impurity of the N atom while the valence band structure generally remains unperturbed compared to pristine 8-ZGNRs. For N-doped 8-ZGNRs, it is observed that the energy bands are non-degenerate at the zone boundary due to symmetry breaking by the impurity of N atom. Mostly they are all converted into n-type semiconductors, which are similar to those of semiconducting CNTs doped with N atom (Yu et al. 2007).

Fig. 1 **a** Schematic of atomic structure of 8-ZGNRs and four different substitutional sites are considered. **b** Schematic of 8-ZGNRs in two probe method for density of states and transmission calculations showing four different dopant positions. The edges are terminated by hydrogen atoms

N atom introduces an impurity level above the donor level, while B introduces below the acceptor level. The donor and acceptor levels are derived mainly from the LUMO and the HOMO of pristine 8-ZGNRs, respectively. However, for N-doped 8-ZGNRs, the electronic state associated with donor level is delocalized. The DFT calculations show that armchair nanoribbons are semiconducting with an energy gap scaling with the inverse of the GNR width (Wakabayashi et al. 1999). Due to the larger covalent radius of B (Koretsune and Saito 2008), the boron–hydrogen bond is stretched and the H atom adjacent to B moves outward from its original position. For the N-doping, the H atom adjacent to N moves inward from its original position. The local structural distortion induced by B-doping is more pronounced than that of N-doping. For B atom, electron-deficient substitution prefers to form in-plane bonding configurations (Wen et al. 2009). The substitutional B atom prefers to lie in the inner of 8-ZGNRs. The DOS for 8-ZGNRs doped with boron and nitrogen atom at different positions are plotted in Figs. 4 and 5, respectively. In N-doped ZGNRs, a very high peak of 31,687 was reported at 2.69 eV while in pristine its value is 86 only. The resulting DOS is showing the appearance of additional sharp states in the conduction band shows the metal–semimetal transition. The distances between N–C and B–C in the relaxed structure are nearly 1.41 and 1.49 Å, respectively. Relaxation of ZGNRs with the substitutional atoms slightly protruding from the ribbon plane always leads to a flat equilibrium geometry, indicating the elasticity of the ribbons. The doped 8-ZGNRs are more inert than the doped semiconducting CNTs, thus suggesting the possibility of developing 1D doped structures with novel physical and device characteristics. The edge substitutional atoms do not result in a shift of the Fermi energy which can be related to the relative position of defect states and the band gap of the pristine ribbon. The N edge atoms are attached to the ribbon with much localized chemical bonds in a sp^3 configuration. This promotes the formation of a deep state in the valence band, which is occupied by the extra electron carried by the N. Moreover, on the contrary, N in the bulk of the ribbon is in a sp^2 configuration. This gives delocalized states in the conduction band. Since no other states are formed in the valence band, the extra electrons coming from N have to be allocated in what was the conduction band of the pristine ribbon, with a consequent shift of the Fermi energy. A perfectly similar consideration can be done for B doping.

The transmission is highly affected by boron and nitrogen doping at different positions in ZGNRs as shown in Figs. 6 and 7. Transmission reduces at all dopant positions near the Fermi level. For pristine 8-ZGNRs, the transmission coefficient is ~2 for energy ≥2 eV and nearly 1 between −2 and +2 eV. For B/N doped at

Table 1 Total energy, Fermi energy, change in total energy, and Fermi energy of pristine and B doped at different positions of 8-ZGNRs

Sample name	Total energy (eV)	Change in total energy (eV)	Fermi energy (eV)	Change in Fermi energy (eV)
1st_position	−1,213.788	79.483	−5.379	−1.509
2nd_position	−1,213.605	79.617	−4.936	−1.066
3rd_position	−1,213.811	79.460	−4.715	−0.845
4th_position	1,213.732	79.540	−4.561	−0.691
Pristine	−1,293.271	–	−3.870	–

Table 2 Total energy, Fermi energy, change in total energy, and Fermi energy of pristine and N doped at different positions of 8-ZGNRs

Sample name	Total energy (eV)	Change in total energy (eV)	Fermi energy (eV)	Change in Fermi energy (eV)
1st_position	−1,406.528	−113.257	−2.343	1.5269
2nd_position	−1,406.056	−112.784	−3.048	0.822
3rd_position	−1,406.300	−113.029	−3.216	0.6537
4th_position	−1,406.209	−112.937	−3.4044	0.4656
Pristine	−1,293.271	–	−3.8700	–

Fig. 2 The electronic structures for 8-ZGNRs doped with one B atom at **a** 1st_position, **b** 2nd_position, **c** 3rd_position, **d** 4th_position, and **e** pristine are plotted, respectively
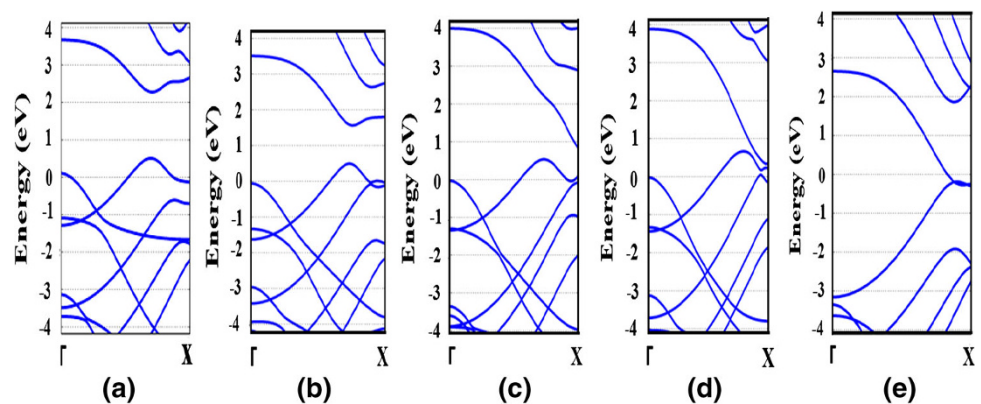
Fig. 3 The electronic structures for 8-ZGNRs doped with one N atom at **a** 1st_position, **b** 2nd_position, **c** 3rd_position, **d** 4th_position, and **e** pristine are plotted, respectively
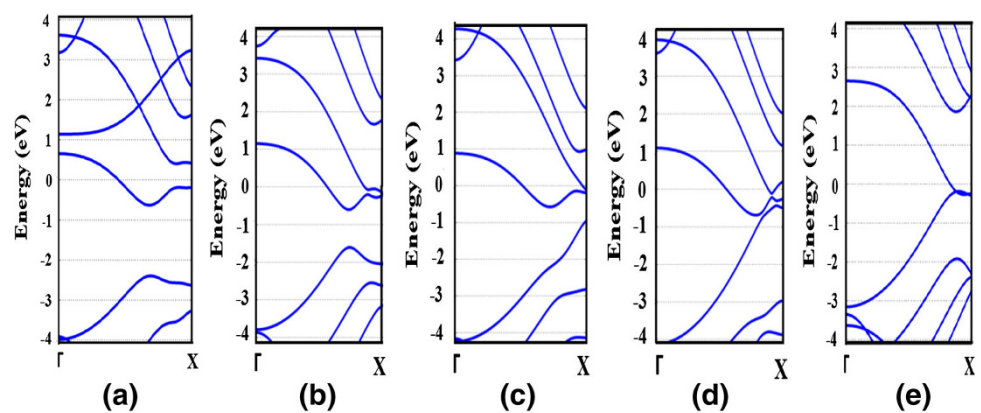
different positions in 8-ZGNRs, the transmission reduces up to zero. However, for B/N doped 8-ZGNRs a sharp increase in transmission is observed near the Fermi level.

These substitutional B and N atoms act as scattering centers for the electronic transport along the nanoribbons. Since transmission is sensitive to B/N doping, our results

Fig. 4 The density of states of 8-ZGNRs for pristine, doped with B atom at 1st, 2nd, 3rd, and 4th positions are plotted
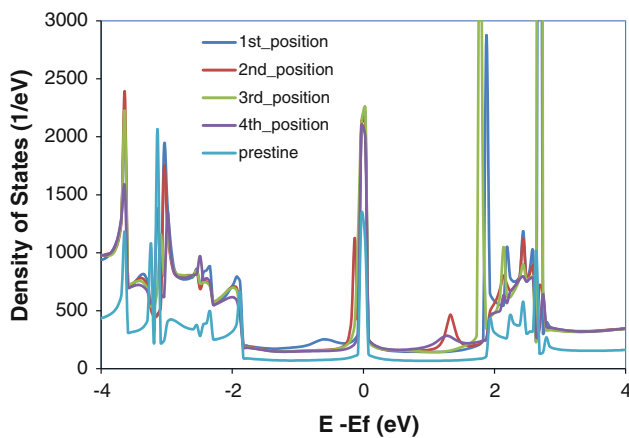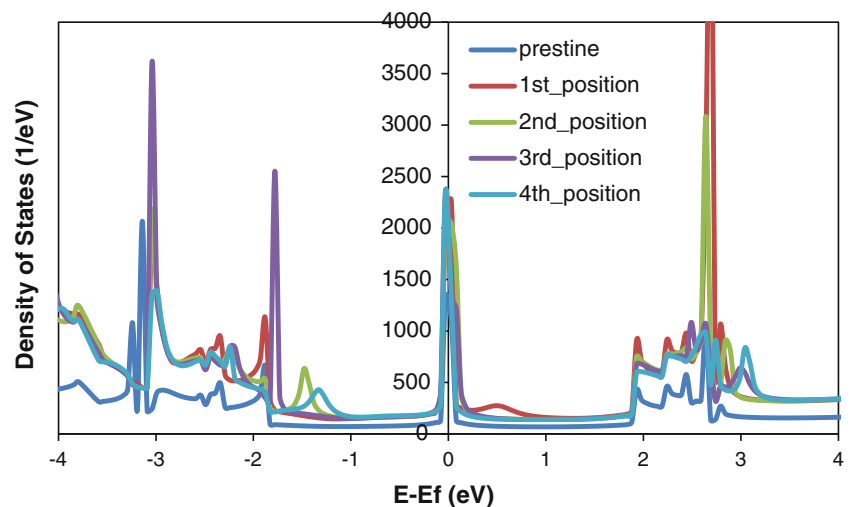
Fig. 5 The density of states of 8-ZGNRs for pristine, doped with N atom at 1st, 2nd, 3rd, and 4th positions are plotted
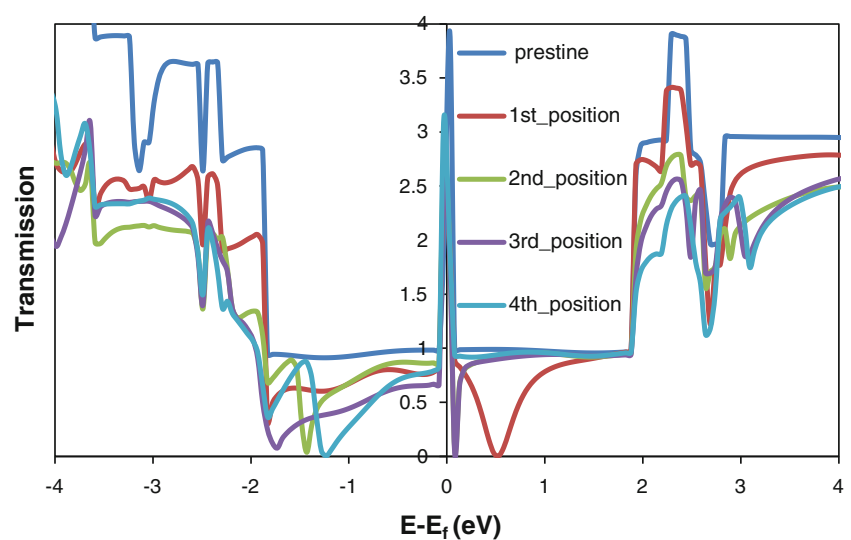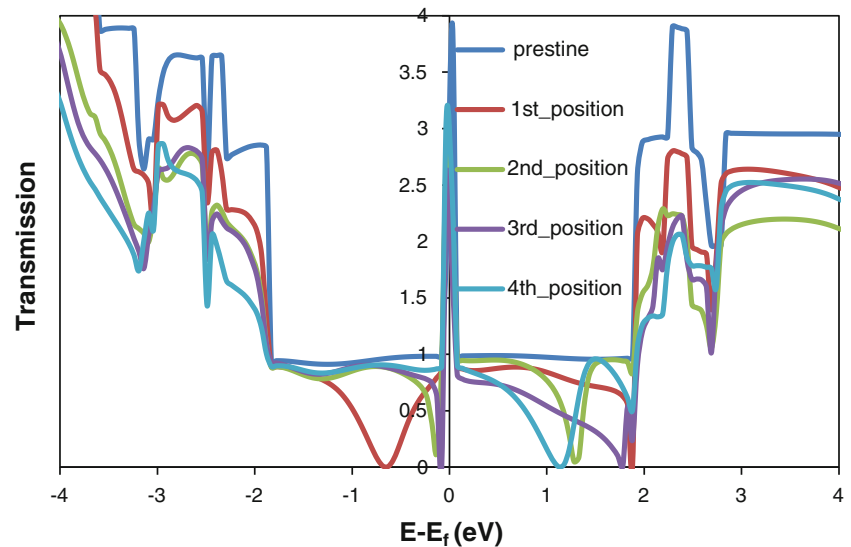
point towards the relative suitability of doped B/N zigzag graphene nanoribbons for nanoelectronics devices.

Conclusions

We predict that the use of nitrogen atoms as substitutional dopants in ZGNRs is energetically more favorable than that of boron atom. The ZGNRs with edge doping of nitrogen atom show n-type behavior while doping of boron atom p-type. The substitutional N atom introduces an impurity level above the donor level while B atom introduces impurity level below the acceptor level. We have also observed that doping of boron and nitrogen in ZGNRs changes the material from metallic to half-metallic or semiconducting. It is also observed that their density of

Fig. 6 The transmission of 8-ZGNRs for pristine, doped with B atom at 1st, 2nd, 3rd, and 4th positions are plotted

Fig. 7 The transmission of 8-ZGNRs for pristine, doped with N atom at 1st, 2nd, 3rd, and 4th positions are plotted

states (DOS) is non-symmetric and their energy band gaps depend on ribbon widths. High-density peaks appearing in DOS curve clearly show the presence of quantum dots in ZGNRs. The transmission is highly affected by boron and nitrogen doping at different positions in ZGNRs. These substitutional B and N atoms act as scattering centers for the electronic transport along the nanoribbons. Since transmission is sensitive to B/N doping, our results point towards the relative suitability of doped B/N zigzag graphene nanoribbons for nanoelectronics devices.

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