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Electronic properties of impurity-infected few-layer graphene nanoribbons

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ABSTRACT

Spurred by achievements in devising different multilayered graphene-based nano-systems, based on the random tight-binding Hamiltonian model and within the coherent potential approximation, the influence of varying the number of layers and the effect of doping by the boron and nitrogen impurities on the density of states of a mono- and few-layer armchair- and zigzag-edge graphene nanoribbons are theoretically investigated. When the nanoribbons are pristine, with increasing the number of layers the band gap of the armchair nanoribbons is decreased, yet the zigzag ribbons remain metallic and depending on the number of the layers few peaks are appeared around the zero-energy level. Moreover, in the presence of impurities, the band gap of the armchair nanoribbons is decreased for each number of layers. The Van-Hove singularities are steadily broadened and the density of states move to a higher (lower) value of the energy as a result of doping with boron (nitrogen) atoms. This study could provide with us to explore and devise new optoelectronic devices based on the impurity-infected graphene nanoribbons with tunable widths and edges.

Graphene is an atom thick allotrope of carbon (**C**) atoms in two-dimensional (2D) hexagonal honeycomb lattice, with unusual electronic properties, owing mainly to its structure [1]. Nanoribbons with a finite width (in the *y*-direction) of graphene (Fig. 1), referred to as graphene nanoribbons (GNRs), have been extensively studied [2–7]. Recent experiments using the mechanical [1,8] and the epitaxial growth methods [9,10] have clarified that it is now possible to make GNRs with various widths. The **C** atoms on the edge of GNRs have two typical topological shapes, namely zigzag (Fig. 1a) and armchair (Fig. 1b). GNRs with zigzag (armchair) edges on both sides are classified by the number of zigzag (dimer) lines across the ribbon width. In the following, *M*-GNR refers to such a prototypical GNR, *M* being the number of zigzag (dimer) lines (Fig. 1). It is predicted that all zigzag GNRs (zGNRs) are metallic while armchair GNRs (aGNRs) are either metallic or semiconductor, depending on their widths [11,12]. In addition, the perfect aGNR gap's, i.e., Δ's, are separated into three categories as $\Delta_{3m} \geq \Delta_{3m+1} \geq \Delta_{3m+2} = 0$ (m is a positive integer number), while the dangling bonds on the edge sites of GNRs will be assumed to be terminated by hydrogen atoms, so the gap of the deformed edge of aGNRs is separated into three groups given by $\Delta_{3m} \geq \Delta_{3m+1} \geq \Delta_{3m+2} \neq 0$ [13].

It is also interesting to study the multilayer GNRs in their own right, as they could help us in understanding the evolution of the electronic structure from graphene to bulk graphite [14–16]. The electronic structure of the multilayer GNRs has been investigated by Sahu et al. [14] using the first-principle electronic-structure method. They have addressed the interplay of magnetism, a perpendicular external electric field, and the energy gap. They found that there are three classes of the energy gap in the multilayer aGNRs, and a strong dependence of the magnetic properties on the edge alignment and the number of layers in the multilayer zGNRs in a vertical external electric field. Using the tight-binding (TB) and Pariser–Parr–Pople model Hamiltonians and at the mean-field Hartree–Fock level, the electronic structure and optical response of multilayer aGNRs, both with and without a gate bias, have been studied by Gundra and Shukla [15]. They result in the optical response depends on the type of the edge alignment and the number of layers.

Since their electronic properties are strongly connected to the delocalized electrons, the GNR systems could be deliberately tuned by proper choosing from different kinds of dopants like the functional groups, adsorbed species, and defect sites [17–21]. In fact, the knowledge of the consequences of doping on the electronic performance of the **C**-based low-dimensional devices is

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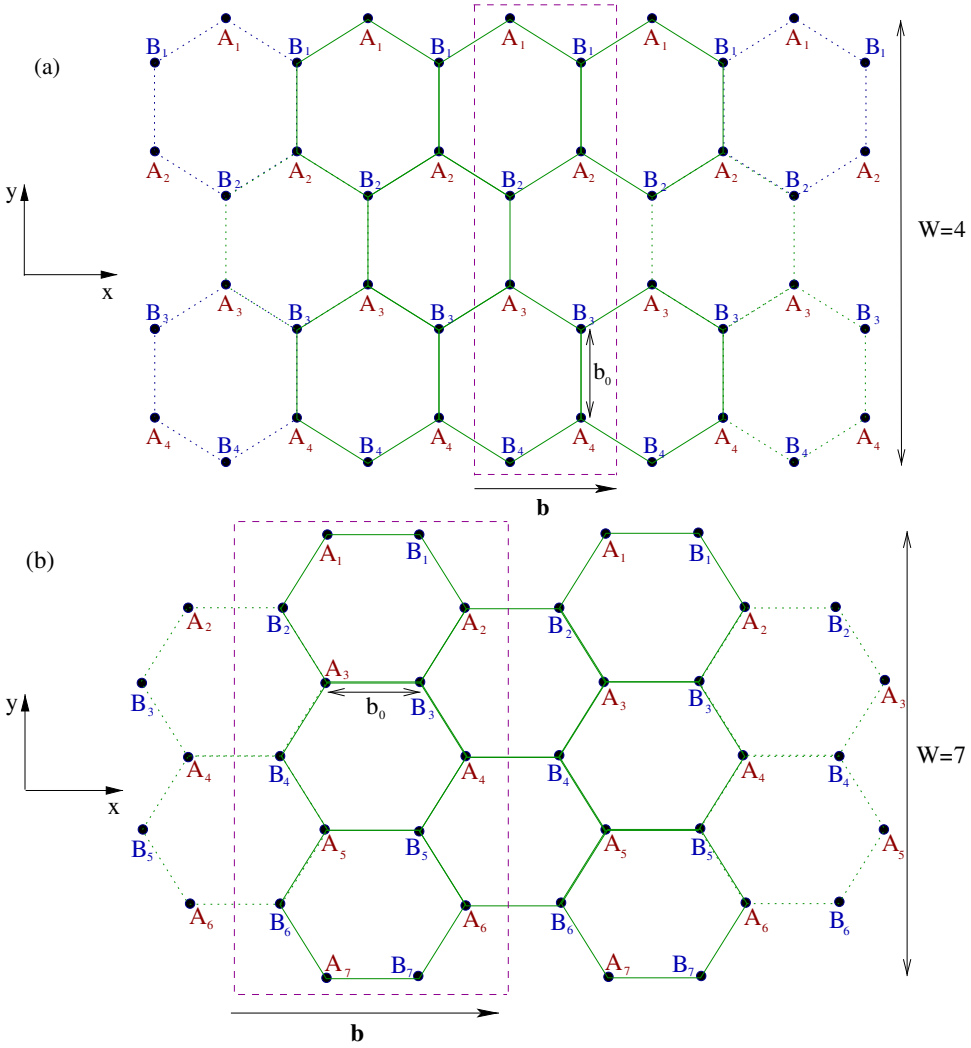

Fig. 1. Geometry of GNRs are shown by (a) panel (4-zGNR) and (b) panel (7-aGNR). The rectangular unit cells illustrate the Bravais lattice unit cells. Each cell includes $N_a = 2$ M sites which are denoted by A_r and B_s where $r, s = 1, \ldots, M$. Primitive vector is pointed by **b** and b_0 is the interatomic distance.

now a key point for future developments of their novel functionalities. The substitution of **C** by atoms with a different number of the valence electrons will thus introduce additional states in the density of states (DOS). Because Boron (**B**) and nitrogen (**N**) atoms differ only by one in their number of the valence electrons compared to the **C** atoms, they are the natural choices as dopants applicable in GNR devices [18,21]. Using nonequilibrium Green's function technique combined with density functional theory (DFT), Padilha et al. [18] have investigated the transport properties of pure and the **B**- and **N**-doped GNRs. Also, using the *ab* initio DFT, the substitutional of one **N** atom per 154 **C** atoms has been performed by Yu et al. [21].

In this study, via implementing the coherent potential approximation (CPA) and based on Green's function formalism of the random TB (RTB) model, we explore the influences of **B**- and **N**-dopants on DOS of mono- and few-layer zGNRs and aGNRs [22,23].

We start with the following RTB Hamiltonian model [22,23] on a quasi-1D lattice (Fig. 1)

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}, \tag{1}$$

where $\hat{\mathcal{H}}_0$ is the TB Hamiltonian model of the pristine ribbon, without **B**- and **N**-atoms, and the random impurity is denoted by the potential $\hat{\mathcal{V}}$. The second quantization form of Eq. (1) is given by

$$\hat{\mathcal{H}} = -\sum_{\alpha,\beta}\sum_{i,j=1}^{N_c}\sum_{p,q=1}^{N_p} t_{ipjq}^{0\alpha\beta}\hat{a}_{ip}^{\alpha\dagger}\hat{a}_{jq}^{\beta} + \sum_{\alpha}\sum_{i=1}^{N_c}\sum_{p=1}^{N_p}\varepsilon_{ip}^{\alpha}\hat{a}_{ip}^{\alpha\dagger}\hat{a}_{ip}^{\alpha}, \tag{2}$$

where α and β refer to the A_r or B_s ($r, s = 1, 2, 3, \ldots, M$) sub-sites inside the Bravais lattice unit cell (Fig. 1), i and j denote the position of the Bravais lattice unit cell in the system, $t_{ipjq}^{0\alpha\beta}$ represents the amplitude for a π electron to hop from sub-site α in layer p of the Bravais lattice site i to the sub-site β in the layers q of the nearest-neighbor site j, $\hat{a}_{ip}^{\alpha\dagger}$ ($\hat{a}_{ip}^{\alpha}$) indicates the creation (annihilation) operator of an electron on sub-sites α in the layer p of the Bravais lattice site i and $\varepsilon_{ip}^{\alpha}$ shows random on-site energy of sub-sites α in the layer p of the Bravais lattice site i due to the presence of the impurities. This takes value of zero with probability $1 - c$ for the host sites (related to **C** sites) and $\eta^{\mathbf{B}}$ ($\eta^{\mathbf{N}}$) with probability c for the impurity sites (related to **B** (**N**) sites) where c is the concentration of the impurities. Also, N_c implies either the number of the Bravais lattice unit cells or the number of the modes in the first Brillouin zone (FBZ), and N_p displays the number of layers in the nanoribbon. In our calculations, we set the chemical potential equal to zero which corresponds to contribution of one electron per p_z orbital in the system. We also take a rectangular real space Bravais lattice unit cell with the primitive vector $\mathbf{b} = b\mathbf{e}_x$ ($\mathbf{e}_x$ is the