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Xiao-Lin Wei,[1,a)] Hui Fang,[2] Ru-Zhi Wang,[2] Yuan-Ping Chen,[1] and Jian-Xin Zhong[1]

[1]*Laboratory for Quantum Engineering and Micro-Nano Energy Technology, Department of Physics, Xiangtan University, Xiangtan, Hunan 411105, China*
[2]*Laboratory of Thin Film Materials, College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China*

First-principles calculations are performed to study the modulation of energy gaps in nitrogen delta-doping (N δ-doping) graphene and armchair-edge graphene nanoribbons (AGNRs). The energy gap of graphene only opens at a large nitrogen doping content. For AGNRs, the energy gaps tend to decrease with the N δ-doping, and an interesting transition from direct to indirect bandgap is observed. Moreover, the effects of N δ-doping on energy gaps incline to decease with the reduction of the doping content. Our results may help to design novel graphene-based nanoelectronics devices by controlling N δ-doping of graphene. © *2011 American Institute of Physics*. [doi:10.1063/1.3609243]

Two-dimensional (2D) graphene has attracted a great deal of interest due to the novel electronic properties.[1] However, its gapless electronic structure limits the applications in nanoelectronics.[2] To modulate the energy gaps of graphene, doping is a good candidate scheme.[3,4] Since nitrogen doping (N doping) can be successfully used to tune the electronic structure of carbon nanotubes (CNTs),[5] studies on N doping graphene[4,6–8] have become a hotspot recently. In these studies, N atoms are adsorbed on the surfaces of graphene or edges of graphene nanoribbons (GNRs), or disorderly substituted into graphene and GNRs. The delta-doping (δ-doping) in which the dopant is confined on the thin layer in the lattice constant provides perfectly ideal conditions to study the doping effect on the host's electronic properties.[9] Recently, the effect of δ-doping on improving electronic properties of semiconductor has attracted extensive attention,[10–15] such as modulating the electron conductance,[11] enhancing the electron mobility,[12] and reducing the turn-on voltages.[15] Therefore, it is necessary to investigate the modulation of energy gaps in N δ-doping graphene and GNRs, which is helpful for not only understanding the intrinsic N doping effect but also designing novel graphene-based nanoelectronic device. However, to the best of our knowledge, there is no study on the N δ-doping effect on bandgaps in graphene and GNRs. In this paper, selecting single N atom chain as δ-dopant, we study the energy gaps in N δ-doping graphene and armchair-edged GNRs (AGNRs) by first-principles calculations. It is found that the energy gaps of graphene or AGNRs can be opened and tuned by N δ-doping. The results may help to design novel graphene-based nanoelectronic devices by controllable N doping.

All calculations have been performed using Vienna *ab initio* simulation package (VASP).[16] The generalized gradient approximation (GGA) (Ref. 17) and the projector augmented wave method (PAW) (Refs. 18 and 19) were implemented. The plane wave energy cutoff is set to 350 eV. The force acting on each atom is relaxed to less than 0.02

eV/Å. For the fully self-consistent calculations of N δ-doping graphene and AGNRs, $5 \times 1 \times 5$ and $1 \times 1 \times 21$ k-mesh using the Monkhorst-Pack scheme[20] are chosen. Subsequently, the non-self-consistent calculations of the N δ-doping graphene and AGNRs are performed with 120 line-mode k-points along the Γ-X-U-Γ path and a denser k-point sampling of 61 line-mode k-points along the axial direction (z) of AGNRs. For the initial atomic configuration of intrinsic graphene and AGNRs, The N δ-doping positions are chosen at the center of the unit cell. The maximum number of the carbon dimer lines n is used to define the configuration of N δ-doping graphene [N-G(n)]. For N δ-doping AGNRs, the dangling bonds on the edge sites are all terminated by hydrogen atoms in order to ensure no contribution to the electronic state near the Fermi level (see the inset in Fig. 1). The ribbon width w denotes the number of dimer lines for AGNRs(w) or N δ-doping AGNRs [N-AGNRs(w)]. The N doping rate is defined by the ratio of N to C atoms in the graphene or AGNRs. The structural relaxation is carried out to locate the equilibrium configuration. To conveniently analyze the band structure and electronic properties, the center symmetry along the x-axis of doped N dimer line should be kept.
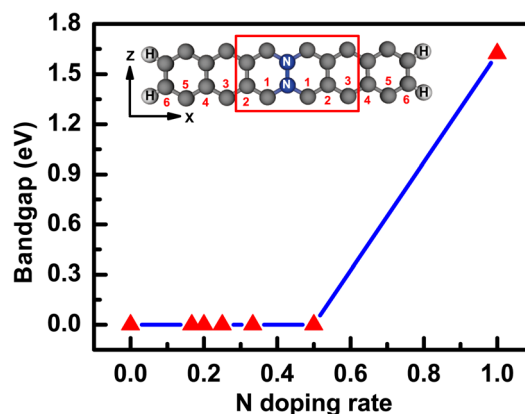

FIG. 1. (Color online) Bandgap in N δ-doping graphene with different N contents. Inset is the schematic diagram of central N δ-doping AGNR. The region in rectangular solid line refers to the unit cell of N δ-doping graphene (N-G(3)).

a)Author to whom correspondence should be addressed. Electronic mail: xlw@xtu.edu.cn.
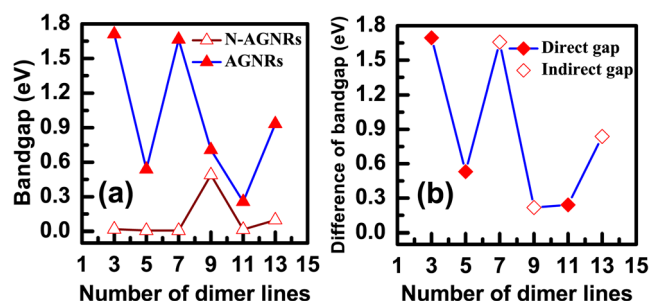
FIG. 2. (Color online) (a) Bandgaps of N δ-doping and intrinsic AGNRs. (b) Difference of bandgaps between N δ-doping and intrinsic AGNRs.

FIG. 3. (Color online) Band structures of N-AGNRs with different width. The shifts (Δk) of the valence band maximum from Γ point indicate the direct to indirect band transition after N δ-doping. The Fermi level is set to zero.

Therefore, the total number of dimer lines of N-AGNRs must be odd.

In Fig. 1, we show the bandgap in N δ-doping graphene with different N contents. The doped N content increases with the decrease of the dimer lines in a periodic cell. It is found that, as the doping content is small, graphene is still gapless. The bandgap of graphene opens only as the N doping rate is 1 and the bandgap is up to more than 1.63 eV. Because of the one more electron in N atom, N doping presents n-type doping properties. In the previous reports, for the graphene with 33.3% N doping content (doped N atom with three neighboring C atoms),[8] the bandgap is about 0.14 eV.[4] In our calculations, the graphene still exhibits metallic behavior even when the N content is up to 25%. These results may indicate that the bandgap of graphene can be opened when the N doping content is more than a threshold value.

In Fig. 2(a), the bandgap of N-AGNR as a function of width w is presented. It is clear that, due to N δ-doping, the bandgaps of the N-AGNRs are smaller than those of AGNRs with the same width. Meanwhile, the change in the magnitude of bandgaps for different families of AGNRs (w = 3p, 3p + 1, or 3p + 2) is also very different. For the N-AGNR (w = 9, 11, 13) with smaller doped N content, the change in the magnitude of bandgap is also smaller. For the N-AGNR (w = 3, 5, and 7) with larger N content, their bandgaps are significantly decreased to zero because of the effect of N δ-doping. This is opposite to N doping effect in graphene. These results may suggest that, due to the quantum size limit of two dimensions in GNRs, the physics of the N doping effect is changed.

In order to clearly show the N doping effect on the change of bandgaps, Fig. 2(b) illustrates the difference of bandgap between N δ-doping and intrinsic AGNRs. It is obvious that, for the same family of AGNRs (w = 3p, 3p + 1, or 3p + 2), the modulation effect of N doping on bandgaps inclines to be weakened with the decreasing N content. More interestingly, for the AGNRs (w = 3p, 3p + 1) with smaller N content, a transition from direct to indirect bandgap can be clearly observed in Fig. 3. For N-AGNR (w = 3p + 1), the N δ-doping induces a shift of valence band maximum from Γ point to Z point. However, the direct to indirect transition in AGNR (w = 3p) can only be achieved by doping smaller N content, and the phase shift (Δk) of valence band edge is less than π. These results explicitly show that not only the magnitude of the bandgap but also the whole electronic structure of the AGNRs can be significantly tuned by the N δ-doping.
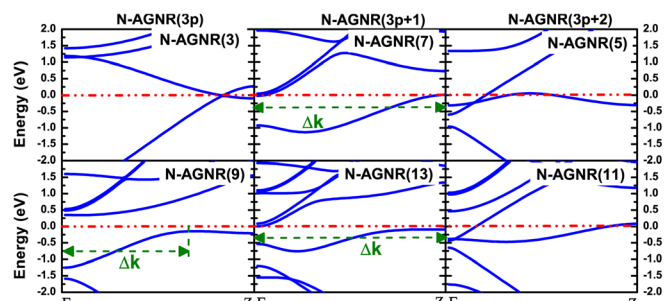
The change of energy gap of N-AGNRs can be explained by the localized states on the N dimer chain. The previous studies[21,22] indicated that the linear defect in the nanoribbons can form a one-dimensional channel along the defect. In our model, the N dimer chain is similar to the linear defect. Thus, a one-dimensional channel will exist in the middle of nanoribbons, which induces a branch of energy band on the band spectrum. The location of the branch determines the AGNRs after δ-doping to be metallic or semiconducting. For the family of AGNRs (w = 3p + 2), the bandgap is small without doping. After δ-doping, the shift of energy band will result in N-AGNRs becoming metallic regardless of the location of the band branch. For the family of AGNRs (w = 3p and 3p + 1), they are semiconducting with wider energy gaps. The location of the band branch is very important. As the branch crosses the Fermi level, N-AGNRs become metallic. Otherwise, they are still semiconducting; however, the branch will induce the transition from direct to indirect bandgap. Recently, Majumdar *et al.*[23] found that a direct to indirect bandgap transition in AGNRs can be induced by a large enough asymmetric external electric field along the width of ribbon. In light of this idea,[23] the direct to indirect bandgap transition induced by N δ-doping can be also partly explained. That is, the transition in N δ-doping AGNRs may be induced by the internal field, which is originated from the mismatch of N-N, N-C, and C-C bond between N and C dimer line. Therefore, our results also provide a new method to modulate both magnitude and type of bandgap in AGNRs by N δ-doping. However, one question is also need to be addressed: How to induce a direct to indirect bandgap transition in the present central symmetric N-AGNRs (symmetric internal field)? Therefore, further investigations on the mechanism of direct to indirect bandgap transition in N-AGNRs are still necessary.

In the present N-AGNRs model, there are five valence electrons for each N atom in the N dimer line and the C with substitutional N could be regarded as a donor in the doped AGNRs. To analyze the extent of n-doping, the shifts of Fermi level between N δ-doping and intrinsic AGNRs have been presented in Fig. 4. It is clear that the offset of Fermi level is similar to the change of bandgap. Moreover, the larger the bandgap, the larger shift the Fermi energy is. The Fermi levels of all N-AGNRs have been shifted into conduction band; it means that the impurity states originated from the N atom centering on the Fermi energy are strongly hybridized with the states of C atoms. It well demonstrates that
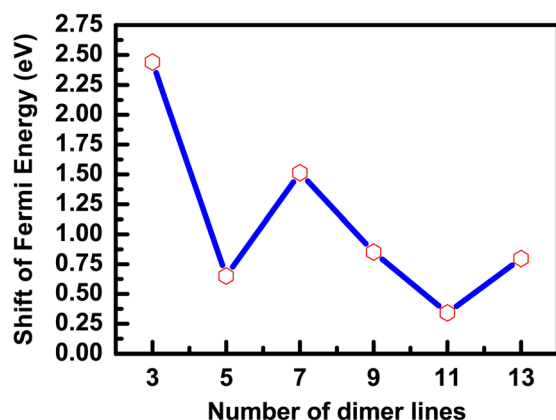
FIG. 4. (Color online) Shift of Fermi level between N δ-doping and intrinsic AGNRs.

the n-type doped AGNRs can be derived from N δ-doping. However, for the family of AGNR (w = 3p + 2) with the smallest bandgap, the relative small shift of Fermi level has been observed in Fig. 4.

In conclusion, the energy gaps in N δ-doping graphene or N-AGNRs have been carefully studied by first-principles density functional theory (DFT) calculations. The results show that, for metallic graphene, the bandgap can be opened by a large enough N doping content. However, for the semi-conducting AGNRs, the bandgap significantly decreases by the effect of N δ-doping. Furthermore, we found that a transition from direct to indirect bandgaps appears in some N-AGNRs. Our results provide a new method to modulate both magnitude and type of bandgaps in AGNRs, which opens up the possibility of new device applications. Nevertheless, to the best of our knowledge, there is no report on how to experimentally implement N δ-doping in graphene or AGNRs. Recently, theoretical investigations showed that the chain like polymeric nitrogen phase can be intercalated in graphene at ambient pressure;[24] experimental studies found that the doped N atom can be substituted for C in graphene. Therefore, it is possible that the single N dimer line (N δ-doping) exists in graphene or GNRs, and it also demon-strates our valuable predictions in N δ-doping graphene and AGNRs.

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