Edge-State-Induced Stacking of Zigzag Graphene Nanoribbons

Taizo Asano* and Jun Nakamura*

Department of Engineering Science, The University of Electro-Communications (UEC Tokyo), 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

ABSTRACT: We have investigated the structural stabilities and electronic properties for AA and the Bernal-stacked AB bilayer zigzag graphene nanoribbons (ZZGNRs) using first-principles calculations within density functional theory. The AB-stacked ZZGNR exhibits the spin-polarized state, while the AA-stacked ZZGNR has the nonmagnetic ground state, being more energetically stable than the AB-stacked one. For the AA-stacked ZZGNR, the interaction between the so-called edge states rather than the van der Waals (vdW) interaction plays an important role: the occupied up-spin and the unoccupied down-spin states at one end of ZZGNR interact with each other, and vice versa at the other end, forming the non-spin-polarized bonding and antibonding states at the zigzag edge. Thus, the structural stability for the AA-stacked ZZGNR is dominated by the trade-off between the edge-edge interaction and the vdW interaction of the basal plane of GNRs.

INTRODUCTION

Graphene, a two-dimensional (2D) sheet of sp²-bonded carbon atoms in a honeycomb arrangement, has attracted enormous attention because of its extraordinary electronic and thermal properties. However, graphene is a zero-gap semiconductor, and thus, many attempts have been made to modulate the electronic properties with an external electric field and heteroatoms for future applications in carbon-based nanoelectronic devices.

Dimension reduction, a fabrication of graphene nanoribbons (GNRs), has also been thought as one of the methods for the modulation of electronic properties of graphene. While in recent years, GNRs have been realized experimentally over the past few decades, a considerable number of theoretical studies have been made on the remarkable structural and electronic properties of GNRs. GNRs have two basic shapes with armchair and zigzag edges. It has been well known that the electronic properties of GNRs depend strongly on edge shapes. Armchair graphene nanoribbons can be either metallic or semiconducting depending on their widths. On the other hand, for zigzag graphene nanoribbons (ZZGNRs), there does not exist a distinct bandgap, and two degenerate flat bands (FBs) appear just at the Fermi level (E_F) within the tight-binding approximation. However, ab initio calculations have shown that ZZGNRs have spin-polarized, antiferromagnetic ground states and that especially a narrow ZZGNR has a finite bandgap. Therefore, ZZGNRs are expected to be magnetic materials and materials for spintronic devices. Such peculiar electronic structures are attributed to the localized state near the zigzag edge, the so-called edge state consisting of nonbonding p_x orbitals.

Recently, the successful fabrication of van der Waals (vdW) heterostructures has opened new ways for band-structure engineering. Very recently, it has been reported that even homostuctures like bi- and few-layer graphenes possess peculiar electronic structures such as superconductors. Furthermore, research studies regarding the interaction between edges as well as interplanar interaction have also been conducted for GNRs, one-dimensional (1D) architectures of graphene. For ZZGNRs having the spin-polarized edge state, the presence of a peculiar stacking structure has been confirmed: two possible stacking fashions, AA and AB stackings, whereas graphite or bilayer graphene has the Bernal stacking. AB-stacked bilayer ZZGNRs are further classified into two types, ABα and ABβ depending on the relative position of their edges, as shown in Figure 1a,b. From the viewpoint of energetics, the AA- and the ABα-stacked ZZGNRs are more stable than the ABβ-stacked one. The AA- and ABα-stacked ZZGNRs have the nonmagnetic ground states, while for the ABβ-stacked ZZGNRs, the antiferromagnetic ground state remains unchanged in each constituent layer. It has been shown by density functional theory (DFT) and tight-binding calculations that the ABα and the AA-stacked ZZGNRs become semiconducting and metallic, respectively. It is noted that AA- and ABα-stacked ZZGNRs have the characteristic structures: the interlayer distance at the edge is quite shorter than that in the central region, whereas the ABβ-stacked one maintains a planar structure, indicating the presence of some edge-edge interaction for the AA- and ABα-stacked ZZGNRs. This means that the structural stability of bilayer ZZGNRs is dominated by not only the vdW interaction in central region but also the edge-edge interaction at the edge.

However, it has not been clarified how the edge-edge interaction is associated with the disappearance of magnetism. In this work, we have investigated the structural and electronic properties of bilayer ZZGNRs and have revealed the stabilization mechanism of the nonmagnetized bilayer stacked ZZGNRs using first-principles DFT calculations in view of the
direct interaction between the spin-polarized states at the edges.

**RESULTS AND DISCUSSION**

Figure 1c shows the optimized structure of bilayer ZZGNRs for the initial structure of AB$^{\alpha}$ with the ribbon width, $N = 6$. This structure has no longer the Bernal stacking, rather an AA-derived one, as described later. On the other hand, the AB$^{\beta}$-stacked ZZGNR maintained the Bernal stacking even after structural optimization. Thus, we hereafter refer to the optimized structures for AB$^{\alpha}$ and AB$^{\beta}$ as AA$'$ and AB, respectively.

Figure 2 shows $E_C$ for bilayer ZZGNRs as a function of the ribbon width, $N$. The values of $E_C$ calculated for the bilayer graphenes with the AA ($-26.2$ meV) and AB ($-29.9$ meV) stackings are also shown by horizontal dashed lines. The AB-stacked ZZGNR decreases with increasing ribbon width and approaches for the bilayer AB graphene monotonically, because the effective number of carbon atoms involved in the interlayer vdW interaction increases with increasing $N$. On the other hand, it can be seen that the values of $E_C$ for the AA- and the AA$'$-stacked ZZGNRs take minimum values. Such peculiar behavior in $E_C$ is attributed not only to the vdW but also to the edge–edge interaction.

It has been well known that the monolayer ZZGNR has the so-called edge state localized near the edge. To reveal the stabilization mechanism of the AA and the AA$'$ stackings, we revisit the electronic structure of monolayer ZZGNRs with a width of $N = 6$ as an example. It has been shown that the antiferromagnetic ground state is more stable than the nonmagnetic and the ferromagnetic states by $61$ meV and $53$ meV per unit cell, respectively, which agrees well with the previous theoretical results. Figure 3a,b shows the band structures of the nonmagnetic and the antiferromagnetic monolayer ZZGNRs, respectively. For the nonmagnetic monolayer ZZGNR, the degenerate flat bands lie just at the $E_F$ in the vicinity of the X point. These flat band states which are degenerate at $E_F$ can gain the exchange interaction energy, resulting in the lifting and the splitting into two bands above and below $E_F$ near the X point ($\Delta E_{FB}$). As a result, the ground state becomes antiferromagnetic. The spatial distribution of the spin densities, $\Delta \rho(r) = \rho^{up}(r) - \rho^{down}(r)$, are shown in Figure 4a for the antiferromagnetic ground state of the monolayer ZZGNR with $N = 6$. As clearly shown in this figure, one sublattice sites are occupied by up-spin electrons and the other ones are occupied by down-spin ones. These states consist of the p$_z$ orbital of carbon atoms and localized near the zigzag edge.

Figure 4b,c shows the optimized atomic structures and spin-density distributions of AB-stacked ZZGNRs ($N = 6$). We can confirm the two types of magnetic arrangements between the layers, ferromagnetic (Figure 4b) and antiferromagnetic.
unoccupied

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represents the energy difference between the occupied and unoccupied flat bands (FB) at the X point.

Figure 3. Band structures for (a) nonmagnetic and (b) antiferromagnetic monolayer ZZGNRs, (c) interferromagnetic and (d) inter-antiferromagnetic AB-stacked ZZGNRs, and (e) nonmagnetic AA- and (f) nonmagnetic AA'-stacked ZZGNRs with the ribbon width of \( N = 6 \). Red and blue lines indicate up- and down-spin states, respectively. The dashed line indicates the Fermi level, \( E_F \). The energy difference between the occupied and unoccupied states is denoted by \( \Delta E \).

The energy difference between these states is negligibly small (\( \sim 3 \text{ meV per unit cell} \)); there is no magnetic interaction between the layers. The interlayer distance is 3.50 Å, which is slightly larger than that of bilayer AB graphene (3.47 Å). Figure 3c,d shows the band structures for the AB-stacked ZZGNRs with interferromagnetic and inter-antiferromagnetic interactions between the layers. As clearly seen in these figures, the degeneracy of flat bands is lifted because of the pseudochemical interaction between the edge states. The most likely explanation is that pseudochemical bonds comprised of the edge-localized \( p_z \) orbitals are formed, leading to the bonding and the antibonding states between GNRs. Figure 5c shows the schematic of interlayer interaction between edge states. The occupied up-spin and the unoccupied down-spin states at one end of GNRs are eligible to interact with each other, and vice versa at the other end of the GNRs, resulting in the non-spin-polarized bonding and antibonding orbitals. The existence of the pseudochemical interaction between the edge states is supported by the following fact: the energy differences between the occupied and unoccupied flat bands, 1.23 and 1.06 eV at the X point for the AA- and AA'-stacked ZZGNRs, respectively, become large compared to that for the monolayer ZZGNR, 0.73 eV. The decrease in the interlayer distance at the edge for the AA- and AA'-stacked ZZGNRs also corroborates the formation of pseudo-covalent bonds between the edge-localized \( p_z \) orbitals. It must be noted that the resonance energy between the \( p_z \) orbitals at the edge is not so large compared with a value for a typical covalent bonding. Indeed, the stacking energies for the AA- and AA'-stacked ZZGNRs \( (N = 6) \) are merely lower than that for the AB-stacked one by 0.109 and 0.116 eV per unit cell, respectively.

We are now ready to consider the difference in the \( E_C \) profile: a minimum \( E_C \) exists for the AA- or AA'-stacked ZZGNRs, while \( E_C \) decreases monotonously as a function of the ribbon width \( N \) for the AB-stacked ones. For the AA- or AA'-stacked ZZGNRs, the value of \( E_C \) is determined not only by the vdW interaction but also by the edge–edge interaction. Since the edge states at opposite edges are weakened mutually by the vdW interaction but also by the edge interaction, the edge–edge interaction becomes large and then \( E_C \) lowers with \( N \). On the other hand, the \( E_C \) value of the AA- or AA'-stacked...
ZZGNRs increases and approaches that of bilayer graphene, because the relative contribution of the edge−edge interaction with respect to the total interaction between GNRs decreases with increasing \( N \). Viewed in this light, the stabilities of the AA- and AA’-stacked ZZGNRs are dominated by the trade-off between the vdW interaction of the basal plane of GNRs and the edge−edge interaction attributed to the edge-localized states. This is the reason why the \( E_C \) profile have minimum values for the AA- and AA’-stacked ZZGNRs.

**CONCLUSIONS**

The structural stabilities and electronic properties of AA-, AA’, and AB-stacked bilayer ZZGNRs have been investigated. For AB-stacked ZZGNRs, each constituent layer maintains the planar structure and exhibits the spin-polarized state, that is, antiferromagnetic state as with the monolayer. On the other hand, for AA- and AA’-stacked ZZGNRs, the interlayer distance at the edge becomes shorter than that in the central region and the nonmagnetic state becomes the ground state. Such changes in the structure and the magnetic ground state are attributed to the pseudochemical bondings between the edge-localized \( p_z \) orbitals: the occupied up-spin and the unoccupied down-spin states at one side of GNRs interact directly with each other, and vice versa at the other side. The resonance energy between the \( p_z \) orbitals is not so large compared with a value for a typical covalent bond; thus, the trade-off between the edge−edge interaction and the vdW interaction of the basal plane of GNRs dominates the structural stabilities for the AA- and the AA’-stacked ZZGNRs. Various terminal functional groups can be available as joining couplers between layers. Our insights will open up a new paradigm in the edge-engineered stacking of 2D materials.

**COMPUTATIONAL METHODS**

We investigated the structural stability of bilayer ZZGNRs with AA, AA’, and AB stackings (see Figure 1), which have widths of \( N \) zigzag chains \((N = 2−12)\) of carbon atoms. Edges of each GNR were terminated by hydrogen atoms. We employed the lattice constant optimized for graphene (2.472 Å) as a unit cell length along the ribbon axis. To avoid interaction between adjacent GNRs in a supercell geometry, GNRs were separated by 15 Å along the other axes. The structural stability of the bilayer system was evaluated on the basis of the stacking energy, \( E_C \):

\[
E_C = \frac{E_{BL} - (2 \times E_{ML})}{n_C}
\]  

(1)
where $E_{\text{bi}}$ and $E_{\text{nl}}$ are the total energies for the bilayer and monolayer systems, respectively. $n_c$ is the number of carbon atoms per unit cell.

We employed the first-principles calculations based on DFT using the Vienna ab initio simulation package\textsuperscript{51} code with the nonlocal vdW correction.\textsuperscript{52} The opt-PBE scheme developed by Klimeš et al.\textsuperscript{53} was adopted as the exchange and correlation energy functional. The cutoff energy of plane wave expansion was taken to be 550 eV. Integration over the 1D (2D) BZ was carried out using 84 k (24 × 24 k) point sampling for ZZGNRs (graphenes). For all models, structural optimization was performed until each component of the interatomic force became less than 5.0 × 10\textsuperscript{-3} eV/Å.

\section*{AUTHOR INFORMATION}

\section*{Corresponding Authors}
*E-mail: asano@natori.ee.uec.ac.jp. Tel/Fax: +81 (0)42 4435156 (T.A.).
*E-mail: junj@ee.uec.ac.jp (J.N.).

\section*{ORCID}
Taizo Asano: 0000-0003-0404-1590
Jun Nakamura: 0000-0001-8909-4645

\section*{Notes}
The authors declare no competing financial interest.

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