Electronic properties of graphene and boron-nitride based nanostructured materials

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Abstract. We study the electronic properties of graphene with periodic structural modifications using the local density approximation within the framework of the density functional theory. It is found that the double-layer graphene with nanotube arrays which connect the two sheets seamlessly is a direct-gap semiconductor. Also the single-layer graphene with periodic holes of 24-atomic-site vacancy is found to have a sizable direct fundamental gap as well. These graphene-based materials should be of high importance for nanoelectronics applications in the future. In addition, we study the electronic structure of the superlattice composed of graphene and boron-nitride layers which are stacked alternately. The material is found to be metallic even though each graphene layer is sandwiched by insulating BN layers and is very far from other graphene layers. The material may show interesting electronic properties being different from those of graphene.

1. Introduction

Ever since the macroscopic production of spherical carbon clusters (C\textsubscript{60} fullerenes) [1], various low-dimensional nanostructured carbon materials have been produced so far: Larger fullerenes such as C\textsubscript{70}, C\textsubscript{76}, and C\textsubscript{84}, carbon nanotubes with different diameters and chiralities [2], and fullerene polymers having one- and two-dimensionally polymerized C\textsubscript{60} networks [3]. Most recently, graphene, the single-layer graphite sheet, was fabricated experimentally via mechanical cleavage [4].

In the case of fullerenes and nanobutes, low-dimensional structural units were produced first, and their bulk solid phases, e.g., solid C\textsubscript{60} and nanobute bundles, were produced later. On the other hand, “solid graphene”, i.e., graphite, has been well known as the ground-state phase of carbon and has been studied for many decades both theoretically and experimentally before the production of its constituent unit, graphene. Therefore, the basic electronic structure of graphene has been known theoretically for decades as well. However, most of the theoretical studies of graphene before its experimental production were carried out in order to understand the electronic properties of graphite. Only a couple of theoretical groups have studied graphene as realistic materials in order to clarify the electronic properties of graphene itself [5] or to design new graphene-based nanostructured carbon materials [6]. In the latter work of ours, three kinds of the periodic structure modifications of the graphene sheet were proposed (figure 1), and their electronic properties were studied in detail using the generalized and transferable tight-binding method. Importantly, most of the periodically modified graphene systems are found to be semiconductors with sizable fundamental-gap values. This is of high
importance from the viewpoint of the nanoelectronics applications of graphene, since the pristine and perfect graphene has metallic transport properties and is not suitable for device materials.

In the present work, we study these periodically modified graphene sheets more systematically in the framework of the density-functional theory, and clarify their energetics and electronic band structures further. In addition, we newly study graphene with regularly spaced holes. Also we report a different kind of graphene-based materials design, i.e. the superlattice of graphene and boron-nitride layers.

![Image](image1.png)

Figure 1 Periodically modified graphene using finite-length carbon nanotubs [6]

2. Periodically modified graphene sheets

In our previous work [6], we proposed three kinds of periodic structural modifications of graphene using finite-length (6,6) carbon nanotubes, which are called open-end (OE), closed-end (CE), and double-sheet (DS) systems according to their geometries (figure 1). It has been clarified using the tight-binding method that most of these OE, CE, and DS nanostructured materials are semiconductors although the structural constituent units, i.e. graphene and (6,6) nanotube both possess metallic electronic structures.

![Image](image2.png)

Figure 2 Electronic band structure of DS(5,0) (left panel). Geometry is shown in the right panel.
In figure 2, the electronic band structure of one of optimized DS geometries, DS(5,0) is shown (see Reference 6 for the detailed definition of the \((n,m)\) indices following “DS”, “OE”, or “CE”). Here, the local-density approximation (LDA) in the framework of the density-functional theory (DFT) is used [7]. As can be seen from the figure, the material is predicted to be a direct-gap semiconductor with the fundamental gap of about 0.4 eV in LDA. Considering the usual underestimation of the fundamental-gap value of semiconductors in LDA, one can expect that this DS(5,0) material should have a sizable gap of about 1 eV. Interestingly enough, the systematic LDA study has clarified that the gap value is inversely proportional to the squared lattice constant of not the original graphene but the superstructure with periodic structural modification [8].

3. Graphene with holes

We also study the periodic modification of graphene using holes, i.e. vacancy clusters using the LDA (figure 3). As for the \(\sigma\) dangling-bond states associated with edge atoms at holes, hydrogen atoms are introduced to terminate them. On the other hand, the \(\pi\) states may possess dangling-bond characters in some cases and may reside around the Fermi level as in the case of one-dimensional graphene nanoribbons [9]. The so-called zigzag edge is found to induce nearly flat-band states just at the Fermi level, giving rise to spin polarization with ferromagnetic coupling along the edge direction while antiferromagnetic coupling between the opposite-side edges.

In this graphene system with holes, it should be note that, due to the presence of the curvature along the circle-shape edge at each hole, it is not straightforward to judge each edge atom to be a zigzag-edge atom or an armchair-edge atom. In the case of the holes corresponding to the 24-site vacancies, all the edge atoms are equivalent as is shown in figure 3. This graphene sheet with the hexagonal-cell arrangements of “V24” holes is found to be a semiconductor having the direct gap at \(\Gamma\) point (figure 4), being similar to the DS structure shown in figure 2. Although all the C atoms in the DS structure possess the \(sp^2\) configuration with three neighbor C atoms and there is no explicit edge atom, this similar gap structure should indicate that opening of the fundamental gap in the two systems might have similar origins. This is an interesting issue to be addressed in the future. In addition, experimental works to introduce periodic geometry modifications into graphene were reported recently [10,11]. The comparative study with experimental reports should be another future important issue in this field.

Figure 3 Graphene with holes of “V24” with \(a=25.3\ \text{Å}\). The width between two holes \(w\) is 15.4 Å.
Figure 4 Electronic energy band of graphene with periodic holes of V24. The spatial distributions of the highest occupied state (at Γ point) and the nearly flat-band state inside the valence band (also at Γ point) are also shown.

4. Superlattice of graphene and BN layers
Recently, based on the DFT energetics, we have designed the superlattice of graphene and boron-nitride layers which are stacked alternately along the direction perpendicular to the layers [12]. It is known that, in the case of graphite, the usual stacking sequence is called “AB stacking” although the “ABC stacking” graphite (rhombohedral graphite) is also known to be present. In the case of hexagonal BN solid, on the other hand, the stacking sequence can be called aa' stacking where below and above each B (N) atom of each BN layer there are N (B) atoms on neighboring layers. Here, capital letters indicate graphene layer configurations while small letters indicate those of BN layers. As for a’ layer, boron atoms are replaced by nitrogen atoms compared with the a layer, and vice versa. Interestingly, the most stable stacking sequence of the alternating graphene-BN superlattice is found to possess Ab stacking (figure 5) where below and above each B atom there always are C atoms on neighboring layers. On the other hand, there are center of carbon hexagons below and above each N atom. Therefore, the B-C interaction is considered to be more attractive than other pairs.

Figure 5 Schematic picture of the Ab-stacking superlattice of alternating graphene and BN layers
This \textit{Ab}-stacking superlattice is predicted to be metallic, although each graphene sheet is sandwiched by insulating BN layers and the graphene-graphene distance is rather long. Moreover, in this superlattice two C atoms in the unit cell are not geometrically equivalent with each other any more due to the effect of the neighboring BN layers, and one may expect the semiconducting electronic properties. These rather unexpected properties might also be due to a rather strong interlayer B-C interaction which might mediate the graphene-graphene interaction in the \textit{Ab}-stacking superlattice. Also it is predicted that \textit{AbAc}'-stacking superlattice should be as stable as the \textit{Ab}-stacking superlattice because in this superlattice the geometry below and above each B (N) atom is the same as those in \textit{Ab}-stacking superlattice.

In the present work, we study the energetics and the electronic structure of the \textit{AbAc}'-stacking superlattice in the DFT. The total energy per atom of this superlattice is actually confirmed to be the same as that of \textit{Ab}-stacking superlattice. Its band structure is shown in figure 6. Interestingly, this newly identified stable superlattice is also found to be metallic, supporting the concept of the strong B-C interlayer interaction proposed previously.

![Figure 6](image)

Figure 6 (a) Electronic band structure of the \textit{AbAc}'-stacking superlattice of graphene and BN layers. Expanded fiture around the KH line is shown in (b).

5. Concluding remarks

Graphene is now the material of the highest interest in nanoscience and nanotechnology due partly to its large potential as a nanodevice material. In order to use graphene to the electronic device in the future, however, in most cases one has to modify its electronic structure from metallic to semiconducting in some way. In this respect, periodic geometry modification of graphene addressed in this issue is of high importance as the systems are found to possess the direct band gap. Also the superlattice of graphene and BN layers studied in this work is to be of high importance in the near future since not only graphene but also monoatomic layer of boron nitride have been produced, and the
superlattice of these two layers will be fabricated soon. Since the stable superlattice of graphene and BN layers is found to be metallic, they may show unique and interesting electronic transport properties in their thin-film phase as in the case of graphene.

Acknowledgments
This work was partly supported by the Global Center of Excellence Program by the Ministry of Education, Culture, Sports, Science and Technology of Japan (“MEXT”) through the Nanoscience and Quantum Physics project of Tokyo Institute of Technology, and also by a Grant-in-Aid for Scientific Research on Priority Area of the MEXT, Japan, Carbon Nanotube Nano-Electronics.

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