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Study on the Energy Band Regulation of the H-BN Doped Graphene Nanoribbons Based on First Principles

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In the present paper, several programs of graphene nanoribbons band gap engineering are simulated and calculated based on the first principles which will be helpful in the experimental progress of graphene energy band regulation. Secondly, we doped hexagonal boron nitride (h-BN) into graphene nanoribbons in the form of super-lattice structure. The results showed that the band gap of super-lattices nanoribbons with zigzag edges or armchair edges becomes larger with increasing BN component. We can regulate the band gap of graphene nanoribbons in the range of 0~2.5 eV in this way, such wide adjusting range will be able to meet the vast majority of the band gap requirements in semiconductor industry.

1. Introduction

In the study of the graphene energy band regulation, scientists first studied the different types of nanoribbons obtained by cropping graphene based on theoretical methods (Qi et al., 2016). Using the tight-binding method under the energy band theory, and considering only the approximation of the interaction of nearest neighbors, the armchair-edge graphene nanoribbons (AGNRs) has a very small band gap. The energy band of the band-shaped graphene can be effectively controlled through this special way of cutting. Its bandgap is opened although in a small range while the zigzag-edge graphene nanoribbons (ZGNRs) still shows zero bandgap. In other words, cropping the graphene into band-like structures with zigzag edges does not change the band structure and does not reach the purposes of opening band gap. With in-depth study, we found that the band gap of the AGNRs is decreasing along with the increase of its width (Nakada et al., 1996), experimental research also confirms this. In the further study of the grapheme band, it is found that the edge structure of nanoribbons has a great influence on its electronic structure (Zheng et al., 2010), some scientists have designed different types of edge structure to achieve the goal of regulating the energy band. Hydrogenation of its edge of purification is a common method in the simulation study (Elias et al., 2009), the study found that the ZGNRs which edge is hydrogen peroxide passivated shows a property of semi-metallic (Liu et al., 2011), and its magnetic properties has changed (Kan et al., 2010). In addition, some scientists cut the GNRs into huge wave-like (Cai et al., 2010), which also have a certain impact on its band structure.

Dope the graphene with other elements while its lattice structure is not seriously damaged. The composition of different substances will inevitably lead to changes in its electronic structure, so that it can achieve the goal of band regulation. Basedon atomic size and electronic structure considerations, the researchers first considered the doping of boron and nitrogen elements. The study of boron doping shows that not only the band gap size will change, but also the spin polarization will occur (Faccio et al., 2010) according to the boron doping amount and the substitution position. The results of nitrogen doping show that the band gap can be opened by 0.2eV (Usachov et al., 2011) the nitrogen atoms have three different binding modes, and different doping methods leading to different results. In the case of co-doping of boron and nitrogen, the functionalized graphene also shows some excellent properties. Graphene and hexagonal boron nitride single atomic layer composite structure is a unique doping of boron nitride. As the hexagonal boron nitride is a wide band gap insulator, its zero bandgap graphite refining compound will make its bandgap change. Related studies also show that this doping way make the graphene bandgap open. In this paper, based on the doping control method, we study on the energy band regulation of the graphene in the way of the hexagonal boron nitride and graphite dilute forming a super-lattice, and summarize the law of band gap change.

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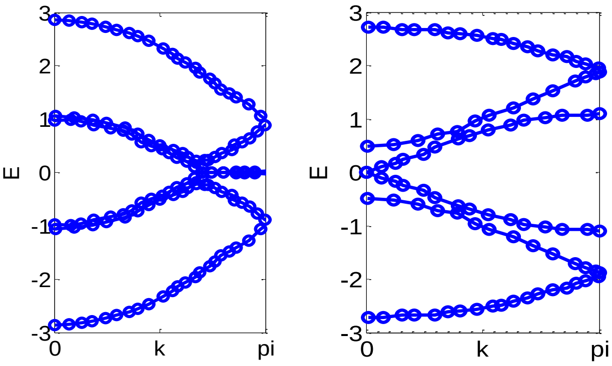
The paper is organized as follows. Methodology is described in chapter 2. In chapter 3 we present results and discussion. Conclusion is given in Chapter 4.

2. Methodology

In recent years, the study of the simulation of material properties based on theoretical calculation is becoming more and more popular. A large number of materials research simulation software also came into being and continuously improved and updated along with the development of materials science. In this paper, we mainly use VASP (Kresse and Furthmüller, 1999; Gungor et al., 2013) to do some work on the GNRs energy band regulation based on the first principles. Figure 1 shows the energy band structure of AGNRs and ZGNRs. In this section, we will provide a brief description of the first principles and the edge effect of GNRs following the computational software used, and will describe the computational methods and model structure.



(a) (b)

Figure 1: (a) Energy band structure of AGNRs; (b) Energy band structure of ZGNRs

2.1 Overview of the first principles

The first principles we usually refer to are highly reliable algorithms using only five basic physical constants: electronic rest mass, electronic charge e, Planck constant h, the speed of light c and glass. It does not rely on any experience of other experiments or semi-empirical parameters during its calculation process.

The first principle is based on quantum mechanics. The core of quantum mechanics is to describe the wave function of particles and its motion equation - Schrodinger equation. As the wave function contains all the information of the system, the starting point of the first principles is solving the Schrodinger equation of the multi-electron system corresponding to the object, thus obtain the other fundamental properties of the total energy and electronic structure of the system.

In order to solve the Schrodinger equation of the multi-particle system, some reasonable simplifications and approximations have been made based on the characteristics of material study. This is the commonly-called three basic approximations implied by first principles calculations: non-relativistic approximation, adiabatic approximation and single electron approximation.

2.2 The edge effect of GNRs

GNRs are quasi-one-dimensional products whose graphene width is limited to less than 100 nm. The special edge effects (such as edge configuration, edge disorder, and different edge treatments) on the properties of GNRs are the most essential different characteristics from graphene, and the source of many of its special properties.

According to the chirality of the lengthwise edge, GNRs can be divided into two kinds of edge configurations: zigzag edge (ZGNRs) and armchair edge (AGNRs).

However, in actual production, it is difficult to obtain such a regular edge, that is, there is a problem of confusion, such as lattice distortion, edge vacancies, jagged edges and armchair-type edge alternately. This kind of edge chaos will cause some errors in the theoretical results, for example the edge disorder will reduce the dependence of the band gap on the orientation effect of GNRs, and also cause other properties of GNRs to decline.

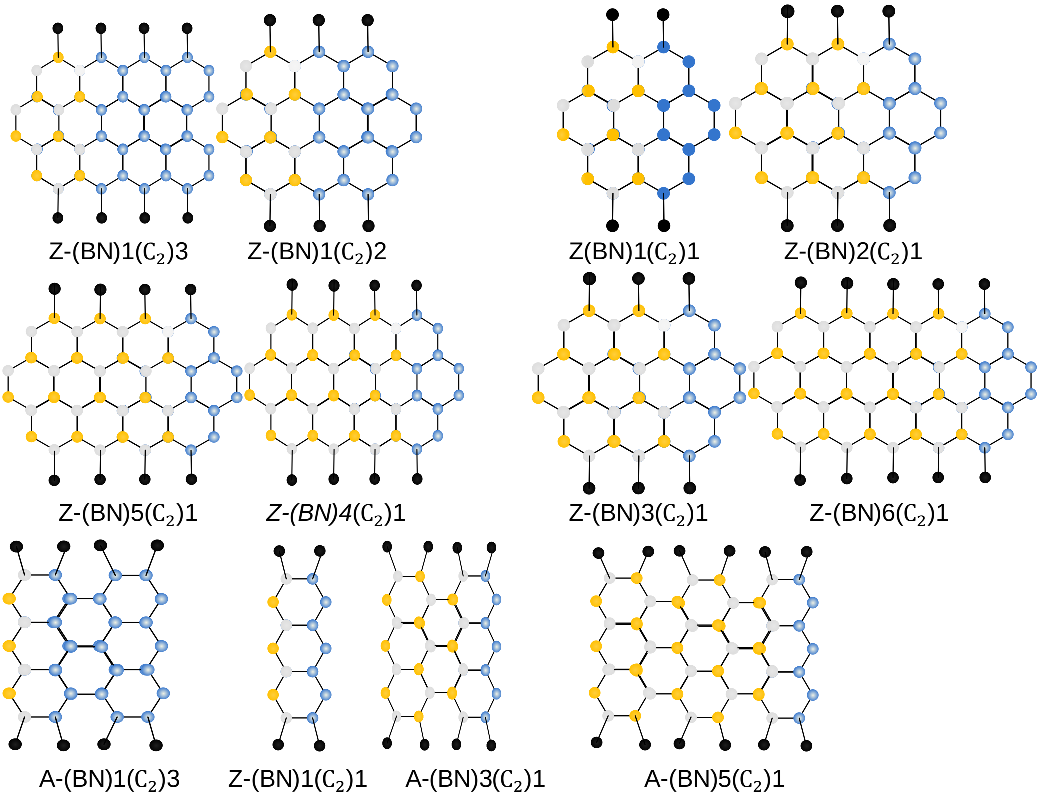
2.3 Introduction ofthe calculation software

In the research process of this paper, two kinds of main softwares are used: Material Studio and Vienna Ab-initio Simulation Package (VASP). Material Studio is used to build the material model. VASP is used to process simulation calculation of the electronic structure of the material properties. In addition, the software VESTA is used to analyze and visualize the charge density during the processing of the calculation results.

2.4 Calculation method and model structure

BN (boron nitride) is a wide band gap ceramic material with excellent characteristics, especially h-BN (Hexagonal boron nitride) with similar structure to graphite. It also has excellent chemical stability and thermal stability as well as intrinsic insulation. Mono-layer h-BN is hexagonal honeycomb structure, and has the same lattice structure with grapheme. Their bond lengths are also similar, so the lattice match is extremely high. Although boron nitride nanoribbons (BNNRs) has the same geometries with GNRs, they have very different properties. BNNRs has a wide band gap, and BNNRs are magnetic. In this paper, the nanoribbons with one-dimensional super-lattice structure are assembled from the fragments of GNRs and BNNRs. By changing the ratio of the two basic structural units (the width of the two fragments) along the KP model direction (Liu et al., 2017) we can control the gap width. The regulatory approach has a huge potential applications of sensors and other nano-electronic devices in the future.

Determining the basic structure of the super-lattice nanoribbons considered, we design the model structure with the Material Studio software, and then derive the parameters of the different shape super-cell structures to be calculated and the atom position coordinates from the model structure, which prepares the POSCAR parameters for the next step with VASP calculations. In the calculations with VASP, all calculations are based on the density functional theory (DFT). In our calculations, the PAW pseudo-potential (Goyal et al., 2016) and the plane wave basis set are used. PBG (Perdew-Burke-Emzerh of) (Lu et al., 2016) is used to deal with the exchange-related interaction energy under the generalized gradient approximation (GGA), the calculation of each step in the plane of the truncation of the energy are taken to 500eV.


Z-(BN)1(C_2)3 Z-(BN)1(C_2)2 Z(BN)1(C_2)1 Z-(BN)2(C_2)1

Z-(BN)5(C_2)1 *Z-(BN)4*(C_2)1 Z-(BN)3(C_2)1 Z-(BN)6(C_2)1

A-(BN)1(C_2)3 Z-(BN)1(C_2)1 A-(BN)3(C_2)1 A-(BN)5(C_2)1

Figure 2: The considered supercell model to be calculated

In the relaxation of the structure, the conjugate gradient algorithm is used to fully optimize the structure, the energy convergence threshold is set to eV, and the force convergence threshold is set to 0.02eV/A. The periodic boundary conditions are used in the supercell structure, and a vacuum layer with a thickness of 15A is provided to eliminate the interlayer effect. We use the Monkhorst-Pack method to generate the integral for the Brillouin zone in the first step, and use the 11×1×1 KPOINTS sampling to correspond to the simple Brillouin zone. Secondly, in the DOS and charge density calculation step, the MP method is used again to calculate the Brillouin zone integral, and the Brillouin zone is increased to 23×1×1. In the third step, KPOINTS is set to linear mode. Since we calculate the one-dimensional super-lattice structure, the high symmetry point of the corresponding compact Brillouin zone is taken as Γ (0, 0, 0) point and χ (0.5, 0, 0) point. In order to get a more detailed band diagram, we take a 30 special points to calculate between the two points.

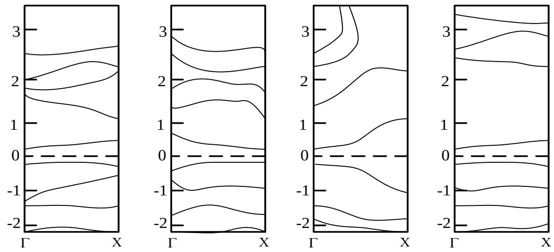
The super-cell models we selected in the calculation are divided into two types: one is the hybrid super-lattice nanoribbons with zigzag edge, which is similar to the ZGNRs in appearance. Both have zigzag-like chain structure in the longitudinal direction. The difference is that a part of the armchair-like chain structure consisting of carbon atoms was replaced by a chain-like structure of boron nitride forming a nanoribbon with a super-lattice structure. The other is the hybrid super-lattice nanoribbons with armchair edge, which is similar to the AGNRs in appearance, the difference is that a part of the chain structure consisting of carbon atoms was replaced by a chain-like structure of boron nitride, and thus a band structure having a periodic structure is obtained. Each chain structure contains 10 atoms. We take such a chain structure as the basic unit, set different ratio of two basic units in different cell models which are shown in Figure 2. As with other computational approaches, the atoms at the edge of the nanoribbons of this hybrid super-lattice structure were also subjected to a hydrogenation purification process.

3. Results and discussion

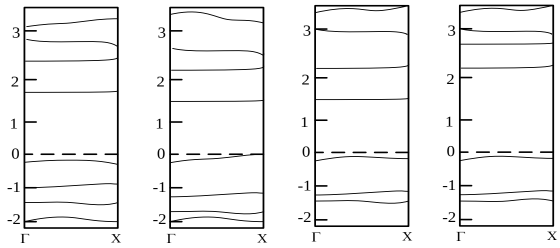
Through calculation, we found that the band gap of the super-lattice nanoribbons depends on the ratio of the two different components in a cell.

Apparently, It can be seen clearly from Figure 3 that the band gap size of the zigzag edge h-BN/grahpene super-lattice nanoribbons or the armchair edge h-BN/grahpene super-lattice nanoribbons becomes larger with the proportion ofBN increases, but the increasing speed is smaller and smaller.

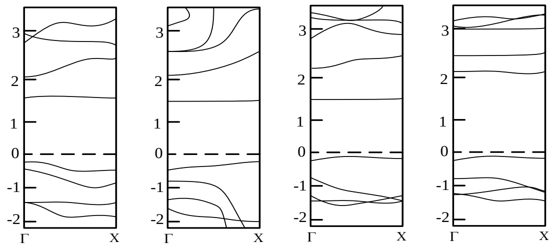
For ZGNRs, it is a non-band-gap semiconductor; and for BNNRs, it is a wide band gap insulator. In a hybrid structure, the increase of the composition of the wide band gap will inevitably lead to an increase in the overall band gap, which also shows that our calculation results in line with the general sense of the laws of nature.



Z-(BN)1(C_2)3 Z-(BN)1(C_2)2 Z-(BN)1(C_2)2 Z-(BN)2(C_2)1



Z-(BN)3(C_2)1 Z-(BN)4(C_2)1 Z-(BN)5(C_2)1 Z-(BN)6(C_2)1



A-(BN)1(C_2)3 A-(BN)1(C_2)1 A-(BN)3(C_2)1 A-(BN)5(C_2)1

Figure 3: Energy band structure

For the band gap size from the band gap map, we perform the correlation calculation according to the output file. In Table I, we give the band gap size corresponding to the super-lattice with different composition ratio.

Table 1: The band gap size of different structures, m/n denotes a super-lattice of different structures marked with Z-(BN)m()n and A-(BN)m()n respectively. Z-Eg and A-Eg represent the band gap size of the zigzag and armchair super-lattice nanoribbons respectively.

m/n	Z-Eg(eV)	A-Eg(eV)
1/3	0.203	0.8228
1/2	0.274	- - - - - -
1/1	0.793	0.9133
2/1	1.679	- - - - - -
3/1	1.914	1.6781
4/1	2.05	- - - - - -
5/1	2.08	1.78
6/1	2.12	- - - - - -

In order to obtain an intuitive display of the data in Table I, we show the band gap of the two different super-lattices and the ratio of the two different components in Figure 4. From the figure we can see that the band gap regulatory range of the h-BN/grahpene super-lattice nanoribbons with zigzag edge is larger than that of the h-BN/grahpene super-lattice nanoribbons with armchair edge. Furthermore, we find that when the band gap is smaller than 1eV, only the h-BN/grahpene super-lattice nanoribbons with zigzag edges could be controlled, which indicates that the edge shapes are selective for the band gap regulation in a small range.

In addition, we can see that the composite nanoribbons and the form of h-BN/grahpene super-lattices show a uniform band gap change trend. It is different with Joo-Hyoung Lee and Jeffrey C. Grossman's graphene and graphane doping result, which band gap change does not have overall uniformity, and the band gap control range is smaller. Therefore, the band gap of graphene material can be effectively controlled in the range of 0-2.5eV by changing the doping ratio of BN.

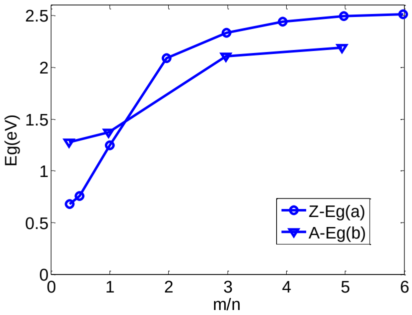


Figure 4: Vand gap and doping ratio

From the point of view of the changing of band structure, the valence band position of VBM (Valence band maximum) is almost invariable with respect to the system, and the opening and widening of band gap is mainly due to CBM (conduction band minimum). The results show that the doping of BN can change the energy level of the system and open the band gap of graphene, and the band gap can be controlled by controlling the doping of BN.

4. Conclusions

In the study of doping regulation, h-BN is doped in the form of super-lattice into the GNRs. Whether edge structure of this hybrid super-lattice is zigzag or armchair, the band gap becomes are lager with the increasing of the doping ratio. The results show that this kind of control method can make the band gap of GNRs continuously adjustable.

Several methods have been developed to control the bandgap of the GNRs, such as edge modification, doping of other atoms, formation of defects and control of the width of nanoribbons. However, those methods can only change the bandgap in a small range; and are also limited by the width. Our graphene band and BN band compositing into a super-lattice structure method can control the band gap in a very wide range (0 ~ 2.5eV), and its bandgap size is almost not effected by the width of the nanoribbons, so that the size of the material can be more miniaturized. Compared to silicon, this graphene super-lattice nanoribbons can make the field-effect transistor scale smaller while ensuring a higher integration ratio, while ensuring a high switching ratio. Band gap of this material combined with a gradient bandgap structure for solar cells, we can improve the photoelectric conversion efficiency due to different wavelengths of sunlight are absorbed. Therefore, this method has more advantages in the practical application of the wider industry.

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