Electronic properties of rippled graphene

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Abstract. Short range periodic ripples in graphene have been modeled. The electronic properties of the rippled graphene have been investigated using first-principles calculations. Compared with flat graphene, there is a band gap opening in rippled graphene. Generally, the value of energy gaps increases as the height of ripples increase, but it decreases as the range of ripples enlarges. The maximum value of energy gaps in rippled graphene can reach several hundred meV, which turns rippled graphene into a good semiconductor. As a result, the magnitude of energy gaps can be tuned effectively by controlling the range and height of ripples in graphene.

1. Introduction

Since the successful isolation of graphene by Novoselov et al [1] in 2004, the prospects of this new material have motivated widespread research. Many interesting electronic properties have been investigated in graphene, such as the anomalous quantum-Hall effect [2-5], the quantization minimum conductivity [6], especially zero effective mass and thus extremely high mobility for electrons and holes [7]. It has become one of the most promising nano-scale materials for building the next generation of electronic devices.

As a unique two dimensional material, graphene has a hexagonal ring structure, which results in $\pi$ bands crossing and a direct zero band gap near the Fermi level [8]. Undoubtedly, absence of band gap sets limitations on its practical applications as a semiconductor. Therefore it is exceedingly important to find methods to effectively open and tune band gaps in graphene.

Researchers have been working on the band gap engineering in graphene for years. Some effective methods were proposed, such as graphene nanoribbons [9] and mesh [10] by making electronic confinements, and graphene oxidation [11] and hydrogenation [12] by chemical treating. However, all above methods introduce additional serious problems, including edge roughness, disorders and impurities, which greatly reduce the carrier mobility in graphene.

Suspended graphene sheets were observed being not perfectly flat showing ripples, with amplitude of about one nanometer [13, 14]. Recent experiments also show that graphene on iridium is slightly rippled [15]. These ripples generate band gaps in graphene by developing spatially varying potentials [16] or effective magnetic fields (also known as gauge fields) [7]. Lau et al [17] demonstrated that periodic ripples can be created and controlled in suspended graphene by thermal treatment, which has been proposed to be a promising way to band gap engineering of graphene by placing it on an especially prepared substrate [18]. Thus understanding the effect of ripples on the electronic properties of graphene is significant for its practical applications in modern nanoelectronics.

In this work, we study the electronic properties of rippled graphene by the first principles method. Our calculation results show band gap opening in the rippled graphene. It is confirmed that electronic transport properties and physical features of graphene can be effectively tuned by controlling the periodic ripple structure in graphene.

2. Simulation methods

We employ the density functional theory (DFT) method implemented in the plane wave basis VASP [19, 20] code that allows the electronic structure of systems with periodic boundary conditions to be calculated.
The projector augmented wave (PAW) [21, 22] potentials and the GGA of Perdew and Wang known as PW91 [23] are adopted. The total energy is converged to within 1 meV with a sufficiently large plane wave cutoff of 500 eV and a Monkhorst-Pack [24] $k$-point mesh of 15×15×1. The structural is fully relaxed until the interatomic forces are less than 0.01 eV/angstrom. In order to eliminate inter-layer interactions, the vertical distance of graphene layers is taken to be 1.55 nm.

Our simulation proceeds by taking a proper super cell as shown in Fig. 1. Periodic ripples are achieved as follows: firstly, pull some specific atoms in the middle part of a super cell up from their original places and fix them; then, relax the rest atoms with fixing their $z$-coordinates in plane to get a final equilibrium structure; plus, the in-plane lattice constants were allowed to relax throughout the simulations. The size of a super cell increases as the range of ripples increases. The amplitude of ripples is defined as the height of carbon atoms away from the original plane, shown in Fig.1 (a). Fig. 1 (b) depicts the curvature of the graphene sheet under the case of pulling out 3 atoms in a 2×2 super cell which will be shown in details later in this paper.

3. Simulation results and discussions

Before doing systematic calculations, we investigate the effect of super cell sizes on the simulation results. Figure 2 shows the value of band gaps as a function of the super cell sizes and the ripple amplitudes, where one carbon atom is pulled up in this case. We can see from Fig. 2 that the value of band gaps increases as the height of out-of-plane atom increases, and decreases not monotonically as the size of super cell increases. It indicates that choosing an appropriate super cell size for the calculations can affect the magnitude of band gaps in rippled graphene. Therefore, it is critical to control the range and amplitude of ripples in graphene for band gap engineering.

Figure 2 The effect of super cell size and ripple amplitude on the opening of band gaps in graphene.

In the following, we will show the DFT calculations of the electronic structures and band gap opening in the rippled graphene systems with 2×2, 3×3 and 4×4 super cells. A regular $k$-points mesh of 60 points has been used to calculate the band structure, and extra 40 points were added near the high symmetry point where the band gap opens. The way to define high symmetry point in band structures can refer to our previous work [25].
The simulation results of the rippled graphene with a $2 \times 2$ super cell are shown in Fig. 3. Figure 3 (a) is band structures of graphene systems with one rippled atom of 0.56 Å and 0.83 Å heights, which show a significant direct band gap at R point. From Fig. 3 (b), we can find that the value of band gaps increases as the height of out-of-plane atoms increases from 0.28 Å to 0.83 Å, and decreases as the number of rippled atoms increases from one to three. The maximum value of band gaps is about 0.93 eV when the height of one rippled atom reaches 0.83 Å.

Figure 3 (a) Band structures for rippled graphene with a $2 \times 2$ super cell. (b) The value of band gaps as a function of the height of out-of-plane atoms.

Then we increase the super cell size from $2 \times 2$ to $3 \times 3$ and do simulations for graphene systems with one, two and four rippled atoms. Similarly, the value of band gaps increases as the height of out-of-plane atoms increases from 0.42 Å to 0.84 Å, and first increases and then decreases as the number of rippled

Figure 4 Band structures for rippled graphene with a $3 \times 3$ super cell. (b) The value of band gaps as a function of the height of out-of-plane atoms.
atoms increases from one to four, as shown in Fig. 4 (b). Fig. 4 (a) displays band structures of graphene systems with two rippled atoms of 0.56 Å and 0.84 Å heights, which show a significant direct band gap at \( \Gamma \) point. As for this 3\( \times \)3 case, the maximum value of band gaps is about 0.64 eV when the heights of two rippled atoms reach 0.84 Å.

We further increase the super cell size to 4\( \times \)4 and do simulations for graphene systems with one, two and four rippled atoms. The calculation results indicate a similar trend as the above two cases. The value of band gaps increase as the height of out-of-plane atoms increases from 0.43 Å to 0.85 Å, and decrease not monotonically as the number of rippled atoms increases from one to four, as shown in Fig. 5 (b). Band structures of graphene systems with four rippled atoms of 0.57 Å and 0.85 Å heights are shown in Fig. 5 (a), which exhibit a significant direct band gap at both K and R points. As for this 4\( \times \)4 case, the band gap of 0.42 eV is maximal when the height of one rippled atom reaches 0.85 Å.

![Figure 5 Band structures of rippled graphene with a 4\( \times \)4 super cell. (b) The value of band gaps as a function of the height of out-of-plane atoms.](image)

4. Conclusions

In summary, we have presented a study on electronic properties of rippled graphene systems by the \textit{ab initio} calculations. Our results show that the maximum value of band gaps decreases as the super cell size increases. Additionally, the band gap increases as the amplitude of ripples increases. A direct band gap of 0.93 eV was achieved, which presents rippled graphene as a good semiconductor. It is consistent with previous experimental work [15, 17] that by controlling the range and amplitude of periodic ripples can effectively tune band gaps in graphene. Although our calculations just modeled a related short range of periodic ripples in graphene, it can be scaled up for the practical prediction.

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