Bandgap Engineering of Graphene by Mean of Adsorption of Defective Graphene

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Abstract

Based on first-principles total-energy calculation, we investigate electronic structures of bilayer graphene one of which layer possesses atomic and topological defects to explore the possibility of band gap engineering of graphene by mean of physisorption of defective graphene. Our calculations show that the pristine graphene layer possesses finite energy gap between bonding and antibonding \( \pi \) states because of the potential undulation caused by the defective graphene. We also found that gap values strongly depend on the defect species and mutual stacking arrangement.

1. Introduction

Electronic structures of graphene sensitively depend on imperfections such as atomic defects, topological defects, and edges. It has been demonstrated that graphene with defects is either a metal or a semiconductor depending on the defect structure and arrangement. Edges with zigzag shapes lead to the spin polarization at edge atomic site because of flat dispersion bands arising from the topologically induced edge localized states [1]. Furthermore, topological defects also induce peculiar electronic states at/near the Fermi level due to the symmetry breaking of AB bipartite network. In addition to the imperfection introduced into the atomic covalent network, interlayer stacking arrangements of graphene thin films also lead to the interesting variations in their electronic structures because of the substantial overlap between \( \pi \) states of adjacent layers. For instance, bilayer graphene are either a metal or semiconductor depending on their interlayer stacking arrangement [2]. Rhombohedral graphene thin films possess a flat dispersion bands around the \( K \) point leading to the ferrimagnetic spin ordering on their outermost atomic layers [3]. These facts imply that the electronic structure of graphene is tunable by controlling the intralayer imperfections and the interlayer stacking arrangements.

In the present work, we aim to investigate the possibility of the electronic structure tuning of graphene by mean of the adsorption of the other graphene possessing atomic and topological defects.

2. Calculation methods and structure models

All calculations were performed based on the framework of density functional theory using the Simulation Tool for Atom Technology (STATE) package. We used the local density approximation for describing the electronic states at/near the Fermi level. These three states emerge at the Fermi level. These three states are found for the bilayer graphene consisting of pristine and defective graphene layers.

In the present work, we consider bilayer graphene one of which layers contains atomic and topological defects. Interlayer spacing is fixed to that of the experimental value of 0.34nm with AB stacking arrangement. For the defects, we consider monovacancy, divacancy, hexagonal vacancy and topological vacancy per 4x4 lateral unit cell of pristine graphene.

3. Result and discussion

Figure 1 shows the electronic structure of monolayer graphene with monovacancies and bilayer graphene consisting of pristine and defective layers. In the case of graphene with monovacancies, three less dispersive bands emerge at the Fermi level. These three states associate with the dangling bond states at the vacancy. We find a pair of dispersive bands just above and below theses states, which possess \( \pi \) state nature. Thus, as for the \( \pi \) electrons, the monolayer graphene with monovacancies has finite energy gap of 1.5 eV.

Similar electronic structures are found for the bilayer graphene consisting of pristine and defective graphene.
containing monovacancies. Although one of two layers retains a perfect hexagonal network structure, the bilayer graphene does not possess a pair of linear dispersion bands at the Fermi level: In the case two additional quadric dispersion bands with the gap of 0.64 eV appear just above and below the three less dispersive bands associated with the monovacancies. The fact indicates that graphene with vacancies can affect the electronic structure of another graphene layer without defects, leading to the semiconducting property with quadric dispersion bands above and below the Fermi level.

Table I, Energy gap between the top and the bottom of $\pi$ bands of pristine graphene adsorbed on defective graphene with the spacing of 0.34 nm.

<table>
<thead>
<tr>
<th>Structure and position of defect</th>
<th>$\pi$ and $\pi^*$ gap [eV]</th>
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<tbody>
<tr>
<td>Monovacancy (per 4x4)</td>
<td>0.64</td>
</tr>
<tr>
<td>Divacancy</td>
<td>0.071</td>
</tr>
<tr>
<td>Dense monovacancy (per 2x2)</td>
<td>0.18</td>
</tr>
<tr>
<td>Hexagonal vacancy (V6)</td>
<td>0.18</td>
</tr>
<tr>
<td>Topological defect</td>
<td>0.15</td>
</tr>
</tbody>
</table>

It is worth to investigate how does the defect species affect the electronic structure of pristine graphene adsorbed on the defective graphene. Our calculation showed that all bilayer graphene do not possess Dirac cone at or near the Fermi level, despite one of two layers retains hexagonal covalent network: two quadric dispersion bands emerge near the Fermi level in addition to the states associated with the defect induced states, indicating that the pristine graphene is not a metal but a semiconductor with finite gap. Table I summarized the energy gap between the top of and the bottom of $\pi$ states distributed on the pristine graphene layer adsorbed on the defective graphene. The gap ranges from 70 to 640 meV depending on the defect species and density. Thus, the gap engineering is possible by adsorbing the defective graphene with controlling the defect species and density.

Figure 2 shows the modulation of the electrostatic potential on pristine graphene by mean of adsorption of defective graphene. As shown in Fig. 2, the potential is spatially modulated in lateral direction with nanometer scale. This potential undulation is ascribed to the inhomogeneous charge density arising from the defects, leading to the modulation on the on-site energy for electrons on C atoms in pristine graphene. Accordingly, the C atoms are no longer equivalent each other, leading to the finite energy gap between bonding and antibonding $\pi$ states.

4. Conclusion

We studied the electronic structure of bilayer graphene consisting of pristine and defective layers using density functional theory with local density approximation. Our calculations showed that all bilayer graphene no longer possess the Dirac cone at or near the Fermi level but quadric dispersion bands together with the states associated with the defects, despite one of two layers retains their hexagonal atomic network. The energy gap between the top and the bottom of $\pi$ states belonging into the pristine layer strongly depends on the defect species, arrangement, and density. The analysis on the electrostatic potential unraveled that the spatial undulation of the potential on the pristine layer arising from the defective layer causes the energy gap. Our findings indicate the possible procedure for tuning the electronic structures of graphene by mean of the adsorption of defective layer with the control of the defect species, arrangement, and density.

References