Exploration of Defect Structures on Graphene

Shansheng Yu* and Weitao Zheng

Department of Materials Science, State Key Laboratory of Superhard Materials, and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, China

For graphene obtained by chemical vapor deposition, there are large amount of defects in the crystalline structures. The carbon atoms from the feedstock can attack the graphene surface in annealing process, which may be one of the reasons affecting the structure of graphene. In order to explore some defect structures on graphene, we investigate the adsorption of carbon adatoms and vacancies on graphene using first-principles calculations. It is demonstrated that the adatoms can form strong covalent bonds with the graphene and the C–C dimmer adsorption may be the most prolific defect model. The C adatom can even fill simple vacancy of graphene. Our numerical simulations also show that the defect structures can lead to the splitting of the mid-gap peak of perfect graphene in the electronic structures. It is suggested that its conductivity would be lower than that of the perfect graphene, which can explain the low mobility of the charge carriers in some experiments.

Keywords: Graphene, First-Principles, Electronic Structures, Defect, Adsorption.

1. INTRODUCTION

Since two-dimensional graphene was obtained successfully in 2004, it had attracted tremendous interests of theoretical and experimental studies. It exhibits fascinating physical properties, and these peculiar properties such as massless high mobility, quasi-particles, and quantum Hall effect make it different from conventional materials. Consequently, graphene is a very promising material for future electronic applications.

An obstacle on the road to graphene devices is the lack of a method for mass production. The chemical vapor deposition (CVD) is a well-known technique for the synthesis of freestanding single- and few-layer graphene (FLG). However, their mobilities are lower than that of the perfect graphene due to defects in the crystalline graphene structures. Hence, the intrinsic properties of graphene have not been achieved. From another perspective, these defect structures may also suggest a complex and interesting behavior. There exists very little knowledge about how defects affect the electronic structure of graphene films obtained by CVD. Vacancies and self-interstitials are main defects in graphitic systems. Though these defects are not favored thermodynamically due to high formation energies, they can be introduced during growth, chemical processing, or irradiation. C adatoms are really self-interstitials in the case of graphene, which have large diffusivity. The growth of FLG films is carried out with CH₄ and H₂ in the CVD chamber, in which CH₄ is carbon feedstock. After the synthesis process, the defects related to hydrogen will be free during the cooling down process, while defects associated with carbon adatoms may be remained. In addition, the intensity ratio of the D and G peaks increase with CH₄ concentration. Therefore, the carbon adatoms coming from the feedstock in the ambient gas can be one of main reasons that affect the graphene surface obtained by CVD.

2. METHODS

In this work, the density-functional theory (DFT) calculations based on first-principles were performed for carbon adatoms on graphene surface, in which the code DMOL3 was used, available from Accelrys Inc. In this code each electronic wave function was expanded in a localized atom-centered basis with each base defined numerically on a dense radial grid. All-electron calculations were carried out with a double numeric plus polarization basis set. For the exchange and correlation term, the generalized gradient approximation was used as proposed by Perdew–Burke–Ernzerhof. Considering the computational limitations, we chose the finite tetragonal supercell graphene (composed of 144 carbon atoms) with periodical boundary conditions in the DFT calculations, and 5 × 5 × 1 k-points in the Brillouin zone were adoped.

*Author to whom correspondence should be addressed.
Because of the low number of the whole atoms (144), the results of electronic structures may be affected in the calculations. For the perfect graphene, when smearing width is 0.003, 0.004, and 0.005, their density of states (DOS) are shown in Figure 1. It is shown that the DOS have oscillations when smearing width is small, and even there is a mid-gap state at the Fermi level. In fact, the position at the Fermi level is just peak of wave in the periodical oscillation, thus it seems that there is a peak state at the Fermi level. When smearing width is large, curve will be smoothed, and it is expected to be linear as a function of energy. However, it is probable that some valuable information near the Fermi level can be covered after the curve has been smoothed. Therefore, the results will be more accurate if the number of atoms is large enough. However, considering our computational capability, we choose the number of atoms is 144 and value of smearing width is 0.003. Though the results of electronic structures will be coarse, we can get useful information through our analysis.

3. RESULTS AND DISCUSSION

We start with the simple model in which a carbon adatom adsorbed on the graphene in Figure 2(a), which is labeled by 1C. It is well known that the equilibrium position of the carbon adatom is a bridge-like structure (the adatom is above the middle of the carbon–carbon bond). In our model, the perpendicular distance between the carbon adatom and graphene surface is 1.79 Å, and the formation energy $E_f$ is 2.62 eV, which agree with the other theoretical results. The DOS are plotted in Figure 2(b). It is shown that the adsorbed structure is not stable due to the exist of sharp states near the Fermi level, which can be attacked by other carbon adatoms easily.

Three possible sites attacked by another carbon adatom are considered in Figure 3(a). When adatom locates at the site of bridge-2, the configuration 2C1 is obtained after geometry optimization, as shown in Figure 3(b), in which there are two pairs of pentagons and heptagons that we refer to as an inverse Stone-Wales defect. This defect has a height of 1.78 Å and $E_f$ of 6.05 eV per adatom. When carbon adatom inserts at the sites of top and bridge-1, the configuration 2C2 containing a protrusive two-atom structure is achieved in Figure 3(c), in which bond length of C–C dimer is 1.28 Å and $E_f$ is 5.67 eV per adatom. Their DOS are shown in Figure 3(d). The mid-gap state of perfect graphene at zero energy (black curve) splits due to the defect. For defect 2C1, there is a pair of shallow levels (labeled by arrows) which are introduced by pentagon–heptagon structures. A heptagon gives up an electron to its neighbors and produces a donor level. Similarly, a pentagon produces an acceptor level. These two levels near the Fermi level indicate that 2C1 defect structure has tendency to interact with other adatoms. In 2C2 configuration, the bond length of C–C dimer (1.28 Å) is between the triple bond (1.20 Å) and the double bond (1.34 Å). An unpaired electron of carbon adatom marked by arrow in Figure 3(c) has been transferred to its neighboring carbon adatom on the graphene surface, which has been taken as an auto-compensation mechanism. A heptagon gives up an electron to its neighbors and produces a donor level. Similarly, a pentagon produces an acceptor level. These two levels near the Fermi level indicate that 2C1 defect structure has tendency to interact with other adatoms. In 2C2 configuration, the bond length of C–C dimer (1.28 Å) is between the triple bond (1.20 Å) and the double bond (1.34 Å). An unpaired electron of carbon adatom marked by arrow in Figure 3(c) has been transferred to its neighboring carbon adatom on the graphene surface, which has been taken as an auto-compensation mechanism.
Fig. 3. (a) Three possible adsorption sites for a carbon adatom on the 1C defect structure are considered. (b) Side and top views of a single inverse Stone-Wales defect (2C1). (c) A point defect with a protrusive two-atom structure on the graphene surface (2C2). (d) DOS for the perfect graphene and graphene containing two carbon adatoms (2C1 and 2C2). Fermi level is set to 0.

When carbon adatoms attack the hillock of 2C1 defect structure, four possible configurations with the amorphous structures at the hillock are presented in Figure 4, which are labeled by 3C1, 3C2, 3C3 and 3C4. Their formation energies are 7.19, 6.34, 6.09 and 6.10 eV per adatom, respectively. Their DOS are shown in Figure 5. It is noted that there are two shallow levels except for configuration 3C1. For configuration 3C1, two pentagons are replaced by two tortuous hexagons due to the broken C–C bond between two pentagons. The remaining heptagons will give up electron to their neighboring structure marked by dashed circle in Figure 4(a), which has also been taken as an auto-compensation mechanism. Hence, the shallow levels will disappear in the electronic structure. However, for other configurations, an inverse Stone-Wales defect is still kept, and adsorbed protrusive two-atom structure does not thoroughly affect the electronic structure. Accordingly, their electronic structures are similar to that of defect 2C1.

The vacancies may also be introduced in the synthesis of FLG films. The formation energy of a single vacancy is calculated to be 7.94 eV. As shown in Figure 6, its DOS is similar to that of 1C defect structure, which also has sharp states near the Fermi level. It indicates that a single vacancy is chemically very reactive, and there is the potential to form a vacancy-adatom pair. Five possible sites near the vacancy are considered in Figure 6(a). After geometry optimization, three atomic structures are obtained, as illustrated in Figure 7. When carbon adatom lies at the sites T1, B2 and B5, the configuration is formed shown in Figure 7(a). Sites B3 and B4 result in Figures 7(b) and (c), respectively. Their formation energies are 6.75, 5.65 and 2.96 eV, respectively. It is shown that configuration in Figure 7(a) is the most preferred, and the deep levels are presented above the Fermi level in Figure 7(d). The configuration in Figure 7(b) has a triangle with height of 1.76 Å whose neighbor is a tortuous heptagon, which leads to two shallow levels similar to that of pentagon–heptagon structures. It is noted that the formation energy of an adatom-vacancy pair in Figure 7(c) agrees with that of the 1C defect structure, and their DOS are also similar. In fact, for the defect structure in Figure 7(b), if a triangle
Fig. 5. DOS for configuration in Figure 4 are plotted, respectively.

stands up out of the FLG films, the reaction barriers should be overcome. Hence, the defect structure in Figure 7(b) is not preferred.

In addition, it is interesting that, when another carbon adatom attacks the areas where two-coordinate atoms lie in the adatom-vacancy pair configuration, as shown in Figure 7(a) (labeled by arrows), the vacancy will be filled. The structure will be transferred to an atomic model of defect structure 1C in Figure 2(a), and there is no barrier in the transformation. The defect structure in Figure 7(c) can be directly observed.18 Due to large diffusivity of adatom, a linear synchronous transit method is used to evaluate the migration barrier of carbon adatom from site B4 to site T1 in Figure 6(a), viz. a transformation from defect

Fig. 6. (a) Atomic model of a single vacancy on the graphene surface. (b) DOS for the perfect graphene and graphene with a single vacancy. Fermi level is set to 0.

Fig. 7. Atomic model of an adatom-vacancy pair on the graphene surface. When carbon adatom inserts at the sites T1 (B2, B5), B3 and B4 in Figure 5(a), the defect structures (a)–(c) can be formed, respectively. Their DOS are shown in (d). Fermi level is set to 0.

Fig. 8. (a) Atomic model of four defect structures 2C2 on the graphene surface. (b) DOS for the configurations containing one (green curve) and four (red curve) defect structures 2C2 on the graphene surface. Fermi level is set to 0.
structure in Figure 7(c) to that in Figure 7(a). The value 1.12 eV of this barrier indicates that the activation of the process requires elevated, but not very high temperature. When the cooling down process is started after the synthesis process, the temperature in the chamber is enough to overcome it. It indicates that some carbon adatoms on the FLG surface can also migrate to the nearby single vacancies to repair them. In addition, defect structure 2C1 in Figure 3(a) is also not favorable compared with defect structure 2C2 due to the same reason as defect structure in Figure 7(b). Therefore, the defect structure 2C2 is the most simple prolific defect model, especially for the FLG films obtained by CVD,\(^{11,12}\) in which there is no electron radiation, and the CH\(_4\) is dilute. The electronic spectra of one defect structure 2C2 (concentration of 0.7% in our model) and four defect structures 2C2 (concentration of 2.8%) compared with the perfect graphene are shown in Figure 8. The attachment of one defect structure leads to the splitting of the mid-gap peak of the perfect graphene. For denser defect structure, an energy gap opens. We suggest that the lower mobility of the graphene achieved by CVD\(^{11}\) is associated with the carbon adatom on the FLG surface.

4. CONCLUSIONS

We have investigated defect structures of the carbon adatom and vacancies on the graphene surface using first-principles calculations. The results show a complex behavior of adatoms and vacancies, and how these defects affect the electronic structures of graphene. C–C dimmer adsorption can be the most prolific defect model on the FLG films. The defect structures can split the mid-gap state of perfect graphene in the electronic structures, thus leading to lower mobility.

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References and Notes


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