Applied Surface Science 257 (2011) 7443–7446

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Density functional theory prediction for diffusion of lithium on boron-doped graphene surface

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ARTICLE INFO

Article history:
Received 3 January 2011
Received in revised form 28 February 2011
Accepted 28 February 2011
Available online 26 March 2011

Keywords:
Graphene
Boron
Potential barrier

ABSTRACT

The density functional theory (DFT) investigation shows that graphene has changed from semimetal to semiconductor with the increasing number of doped boron atoms. Lithium and boron atoms acted as charge contributors and recipients, which attracted to each other. Further investigations show that, the potential barrier for lithium diffusion on boron-doped graphene is higher than that of intrinsic graphene. The potential barrier is up to 0.22 eV when six boron atoms doped (B_6C_{26}), which is the lowest potential barrier in all the doped graphene. The potential barrier is dramatically affected by the surface structure of graphene.

1. Introduction

Develops lithium-ion batteries largely depend on the advancement of the new materials of battery electrode. Currently, graphite and various carbon nano-materials are basically used as anode material for lithium ion batteries. However, it is not an ideal host material because of the decrease in specific capacity for graphitic anodes [1]. Recently, carbon nano-material has attracted a wide range of applications in lithium storage, such as carbon nanotubes, fullerene, and graphene [2–11]. The investigation has shown that doping with impurities may allow tuning of the properties and chemical sensitivity of carbon nanostructures [5–9]. The doped carbon nano-materials have displayed superior Li adsorption capabilities. For example, the BC_3 tubes are promising candidates for Li intercalation materials in boron-doped carbon nanotubes [10]. B-doped graphene can form Li_6BC_5 compound after Li-ion adsorption, which corresponds to a lithium storage capacity of 2271 mAh/g [11]. To improve the reversible capacity and cycling stability, we should be concerned about the diffusion of lithium on the surface of these materials. Zhou et al. [10] have found the energy barrier for Li diffusion inside (8, 0) carbon nanotubes to about 0.11 eV. But when diffusion takes place inside boron-doped carbon nanotubes, (BC_3) the energy barrier reaches to about 0.08 eV. In graphene, the energy barrier is 0.15 eV [12].

Recently, Panchakarla et al. synthesized the boron and nitrogen doped graphene [13], and Wang et al. [11] found that the boron-doped graphene dramatically improved lithium ion storage theoretically. But how many boron atoms should dope in, and the size of potential barrier for lithium diffusion on boron-doped graphene is not clear. Therefore, we will study the electronic structure of boron-doped graphene, and analysis of the potential barrier of lithium diffusion on different number of boron-doped graphene in this article.

2. Computational method

First-principles calculations are performed within the DFT, and the exchange and correlation functional is provided by the version of Perdew-burke-ernzerh in the generalized gradient approximation (GGA) [14]. All calculations were performed with the VASP (Vienna Ab initio Simulation Package) [15–17] software package. The program uses periodic boundary conditions and a plane wave basis with cut-off energy of 400 eV. A supercell 4×4 containing 32 atoms is used to research the interaction of the Li with graphene. We used a vacuum space of 13.4 Å to avoid interactions between adjacent layers. The sampling of the Brillouin zone was done with a $9 \times 9 \times 1$ Mockhorst–Pack (MP) grids [18]. The structure of the Li–B–graphene system was fully optimized, and the relaxation will stop if all forces are smaller than 10^{-3} eV/Å.

3. Results and discussion

The structures we designed containing 32 carbon atoms, doped with one (BC_{31}), two (B_2C_{30}), six (B_6C_{26}), and twelve ($B_{12}C_{20}$) boron atoms respectively (see Fig. 1). The optimized in-plane

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doi:10.1016/j.apsusc.2011.02.135

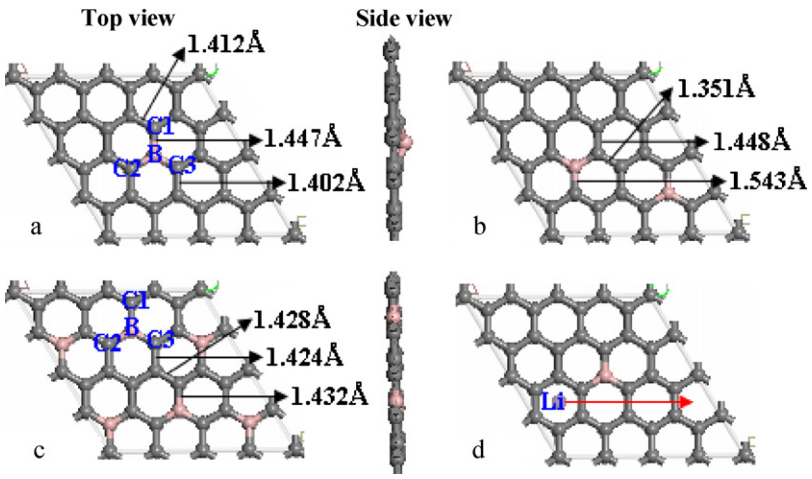

Fig. 1. Schematic map of boron-doped graphene: (a–c) illustrate the one, two, six boron atoms doped graphene, (d) diffusion of Li on a typical one-dimensional path.

lattice constant of pristine graphene is 2.459 Å, which is close to the experimental value of 2.46 Å. The relaxed lattice constant of B-doped graphene increases with the number of doped boron atoms increasing due to the covalent radius of boron is larger than carbon atom.

First, the electronic properties of intrinsic and boron-doped graphene were investigated using pristine graphene, BC_{31}, and B_6C_{26}. As shown in Fig. 2(a and c), the density of states (DOS) of B-doped graphene shows that compared with the original zero-band gap graphene, the band gap of B-doped graphene becomes larger with increasing the number of B doping. In addition, the partial density of states (PDOS) of P_x and P_z orbital are broadening gradually while the peak value decrease [depicted in Fig. 3(a and c)]. The P_y orbital mainly act as a frontier molecular orbital, except for the PDOS near the Fermi level separating gradually, there are no other noticeable changes. After Li adsorption on boron-doped graphene [see Fig. 2(d–e)], the band gap of one, six boron-doped graphene are 0.54 eV, 0.87 eV, respectively, which are slightly smaller than that of the pre-adsorption of lithium. From Fig. 3(d–e) we can see the PDOS of P_x and P_y orbital increases with the increasing number of boron, and the peak value is as high as 0.79 with six boron atoms doping.

Second, the change of the Fermi level is an important index to measure the charge loss of the system. However, when doped with

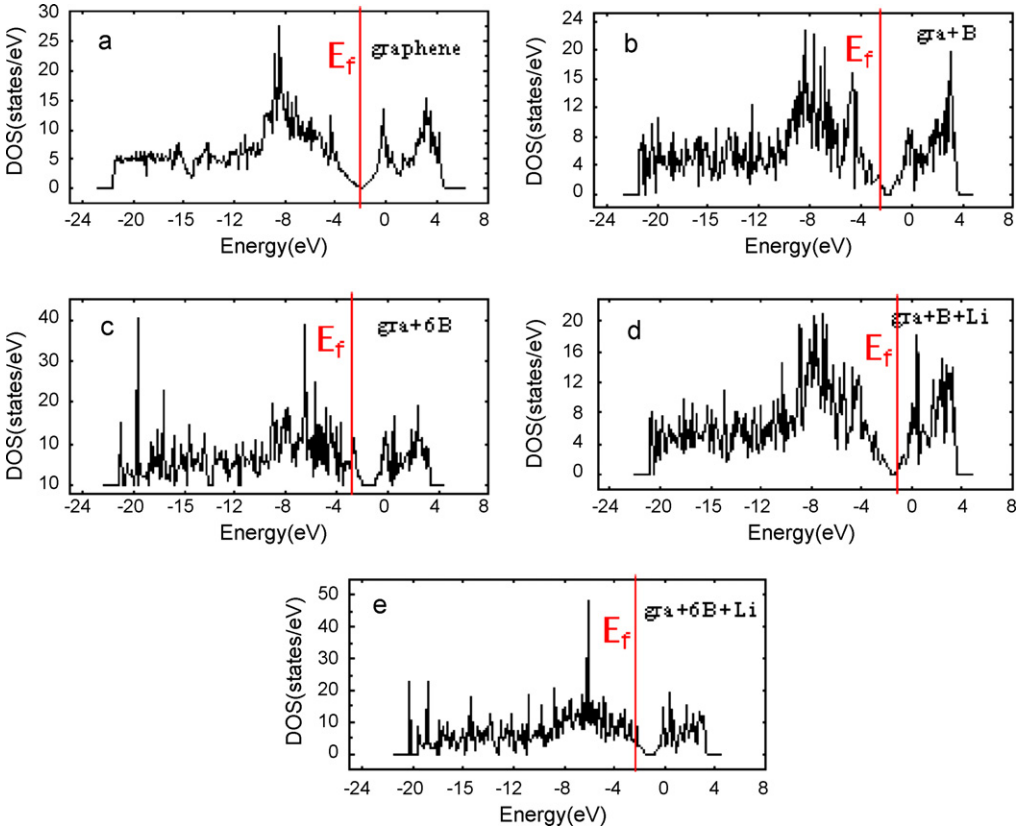

Fig. 2. The total DOS of the pristine graphene, boron-doped graphene, and the case where Li atom are adsorbed: (a) intrinsic graphene, (b and c) correspond to BC_{31}, B_6C_{26}, (d and e) correspond to $LiBC_{31}$, LiB_6C_{26}, respectively.