First-Principles Study on the Graphene Adatom and its Dimer*

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The stabilities and atomic geometries of the graphene adatom and its dimer are studied using first-principles calculations based on the density functional theory. In the most stable structure, the adatom is located above the bond-center site. We also found a metastable structure whose formation energy is slightly (0.25 eV) higher than the most stable structure. The diffusion barrier of the adatom is estimated to be 0.44 eV. Then, dimers are expected to be formed by the diffusion of the adatom. The dimer has three stable structures whose formation energies are close to each other. Since the dissociation energies of these structures are large (5.90-5.93 eV), the dimers are energetically stable. Therefore these structures are expected to be detected under some experimental conditions. [DOI: 10.1380/ejssnt.2008.269]

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I. INTRODUCTION

Carbon nanomaterials have attracted much attention since they are candidates for post-silicon devices. To produce nanodevices, the control of defects is very important as in the case of silicon technology. Compared with conventional silicon devices, the effects of defects are expected to be serious because of the low dimensional conductivity. Therefore, the study of defects in carbon materials is undertaken. Thus far, pentagon-hexagon pairs [1], monovacancies, multivacancies [2–8], adatoms [9, 10], adatom dimers [11], and adatom-vacancy pair [12] have been studied. In particular recent high-resolution transmission electron microscopy was used to directly observe the atomic defects in graphenes [13].

The adatom and vacancy are fundamental intrinsic defects and are extensively studied in the field of semiconductor materials. However, the understanding of these defects is still insufficient in the fields of carbon nanomaterials. Early experimental studies on graphite indicate that the monovacancy is mobile in the temperature range of 1000-1400 K and the activation barrier is 3 eV [14]. However, first-principles calculations show that the activation energy is much smaller (1.7 eV) [4]. The reason for the discrepancy between experimental results and theory is unclear. The activation energy of adatom diffusion in graphene was experimentally estimated to be 0.1 eV [15], which differs from the value estimated by first-principles calculation (0.47 eV) [10]. Therefore, studies on fundamental defects are still insufficient.

In a previous paper, we reported the most stable structure of graphene adatom and its aggregation [16]. In this paper, we focus on the adatom and its dimer, and we calculate formation energies of their several geometries. In both cases of adatom and its dimer, we found metastable structures whose energies are close to those of the most stable structures.

In our first-principles calculations, we use the generalized gradient approximation (GGA) within the density functional theory (DFT). A previous study revealed that the adatom has a magnetic moment but the energy difference between the GGA and the spin-polarized GGA is very small [10]. Because our purpose is to reveal the stability of the defects, we neglect the spin polarization. Ultrasoft pseudopotential and the plane wave basis set whose maximum kinetic energy is 25 Ry are used. In the optimized geometry of graphite, the bond length is 1.42 Å, which is the same as the experimental value (1.42 Å) for the graphite.

We use the 128-site supercell with the rectangle shape of the 17.04 × 19.68 Å² size. This size corresponds to the pristine supercell. The sampling point in the two-dimensional Brillouin zone integration is 4. We calculate the formation energy, which is the difference between the total energy of the defect system in the supercell and the multiplication of the energy of the perfect graphene sheet per atom and the number of the atoms in the supercell.

II. THEORETICAL METHOD

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III. RESULTS AND DISCUSSION

A. Adatom

Here we start to carry out calculations on the adatom. In the most stable geometry, the adatom is located above the bond center site [Fig. 1(a)]. This adatom has two bonds whose length is 1.53 Å each, which is close to that of the diamond crystal bond (1.54 Å). The length of the bond connecting the two nearest neighbor atoms is 1.54 Å and the bond angle of the adatom is 60.1°. The two nearest-neighbor atoms are four-fold coordinated and they are located 0.28Å above the graphene plane. The formation energy of this defect is found to be 6.33 eV.

We next study the diffusion barrier of this adatom by using a constrained optimization method. In the transition state, one of the two bonds of the adatom in the most stable structure is broken [Fig. 2], and the length of the remaining bond is 1.49 Å, which is somewhat shorter than that of the most stable structure (1.53 Å). The difference between the total energies of the most stable and
The transition structure is 0.44 eV which correspond to activation energy of the adatom diffusion. This value is close to the results of the previous spin-polarized GGA (0.47 eV). We also perform calculation based on the local density approximation (LDA) and find that the calculated activation energy is 0.33 eV, which is substantially lower than that calculated from the GGA. The LDA tends to underestimate the activation energy, so we expect that the results based on the GGA is more reliable.

In any case, the theoretical values are higher than the experimental one (0.1 eV) [15]. The discrepancy between the theoretical and experimental energies suggests that the rather-old-experimental value [15] should be carefully reconsidered.

We also find a metastable structure whose formation energy is slightly (0.25 eV) higher than that of the most stable structure [Fig. 1(b) and (c)]. In this metastable structure of the D$_{3h}$ symmetry, the adatom has three bonds to the graphene atoms. One graphene atom is displaced from the graphene plane in the opposite direction of the adatom and becomes equivalent to the adatom. This atom also has three bonds to the graphene plane. The bond lengths are 1.57 Å and the bond angles are 96.1°. When the graphene is located on a substrate such as SiO$_2$ and SiC, this metastable structure may have higher energy or become unstable because one carbon atom is below the graphene plane. On the other hand, this defect has an energy close to that of the stable geometry in the case of carbon nanotube having a large radius.

Electron irradiation experiment is expected to create adatoms by kicking out graphene atoms. Our calculation suggests that two structures having similar formation energies are formed by electron irradiation experiment. So, two kinds of activation energies may be observed.

### B. Adatom dimer

Next, we study the dimer of adatoms since the dimer is expected to be formed during the diffusion of the adatom. We found three stable structures. The most stable structure is shown in Fig. 3 (a). The dimer is located above the bond-center and has two bonds with the graphene plane. The lengths are found to be 1.58 Å whereas the dimer bond length is short (1.28 Å). The two nearest-neighbor atoms are located 0.16 Å above the graphene plane. The formation energy of this defect is found to be 6.74 eV.

We also found two metastable structures whose formation energies are slightly (20-28 meV) higher than that of the most stable structure. An optimized metastable structure is so called 7-5-5-7 defect shown in Fig. 3(b). In this metastable structure, two heptagons and two pentagons are formed, and thus all the atoms are three-fold coordinated. As previously reported [16], the total energy is substantially lowered when the length of the unit cell in the y-direction is slightly larger. So, we optimize the unit cell and find that the length of the unit cell in the...
y-direction becomes 1 % longer. The dimer bond length is 1.43 Å whereas the bond between the dimer and the graphene atom has the length of 1.41 Å. So these bonds have $sp^2$ hybridization characters. The formation energy of this structure is found to be 20 meV higher than that of the most stable structure. In another metastable structure, the dimer has one bond with the graphene plane [Fig. 3 (c)]. The dimer bond length is 1.28 Å and the bond between the dimer and a graphene atom is 1.53 Å. The formation energy is 28 meV higher than that of the most stable structure.

We conclude that three atomic structures of the dimer have almost degenerated formation energies. Through diffusion of the adatom, these structures are expected to be formed. The energy required for the dissociation of those dimers into two adatoms (Ad$_2$ $\rightarrow$ 2Ad) is very high (5.90-5.93 eV). Therefore, once these structures are formed, they are expected to be stable. Therefore, we expect that these structures are observed under some experimental conditions.

Electron irradiation experiment is expected to create adatoms as was mentioned. Under some temperature conditions, adatoms diffuse and the dimer is expected to be created.

IV. SUMMARY

Performing first-principles calculations based on the GGA within DFT method, we studied the atomic structures of an adatom and its dimer, and found their most stable and metastable structures. In the most stable structure, the adatom is located above bond-center site. The activation energy of the adatom diffusion is 0.44 eV. We also found a metastable geometry of the $D_{3h}$ symmetry. Both metastable structure and the most stable structure may be formed by the experiment of electron irradiation. Therefore two kinds of the activation energies are expected to be detected. The dimer has three stable geometries whose formation energies are close to each other. In the most stable structure of the dimer, the dimer is located above the bond-center site. The energy required for the dissociation of the dimer into two adatoms is very high (5.90-5.93 eV). Therefore, these structures are expected to be stable. Our studies suggests that these structures are formed under a certain experimental condition.

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