

First-Principles Calculations of Hydrogen and Hydrogen-Vacancy Pairs in Graphene

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We study mono-hydrogen and hydrogen-vacancy pair in graphene by using first-principles calculations. In the most stable structure of mono-hydrogen, the hydrogen atom is bonded to one of the carbon atoms in the graphene sheet. The energy of the most stable spin-polarized state is 80 meV lower than that of the nonmagnetic state. We also study the hydrogen mono-vacancy pair. The dissociation energy of this pair into mono-vacancy and mono-hydrogen in graphene is positive (3.0eV). Therefore, when hydrogen diffuses, this complex is expected to be formed and this pair is nonmagnetic.

Key words: Graphene, Hydrogen, Density Functional Theory, First Principle Study, Generalized Gradient Approximation.

1. 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 [1].

It is well known that graphene has novel electronic properties. It has no band gap and there are so called Dirac cones at the k point where the Fermi level is located.

Hydrogen is a common impurity in graphene [2-4]. Therefore it is important to clarify how the hydrogen impurity affects the electronic properties of graphene. Meanwhile the mono-vacancy is one of the fundamental intrinsic defects. It is expected to be mobile at only high temperatures. Then, under the condition that hydrogen diffuses, the hydrogen mono-vacancy pair is expected to be formed.

In this paper, we perform first-principles calculations of mono-hydrogen and hydrogen-vacancy pair on graphene. Since the magnetism plays an important role in defects and impurities, we perform spin-polarized density functional calculations.

2. COMPUTATIONAL METHOD

By using the code PHASE [9], we perform first-principles calculations based on the density functional theory (DFT). We use a slab model where the spacing of the slab is 6.71 Å. Each unit cell contains 72 atomic sites and its size is 13.62 Å × 11.36 Å. The sampling k points are 2 × 2 × 1. We use the ultrasoft pseudopotential and the maximum kinetic energy of the plane waves is 25

Rydberg. The cut off energy for the charge density is 230 Rydberg.

3. RESULTS AND DISCUSSION

3.1 Hydrogen on graphene

First we carried out calculations on the mono-hydrogen atom on graphene. In the most stable geometry, the hydrogen atom is bonded to a carbon atom (Fig. 1).

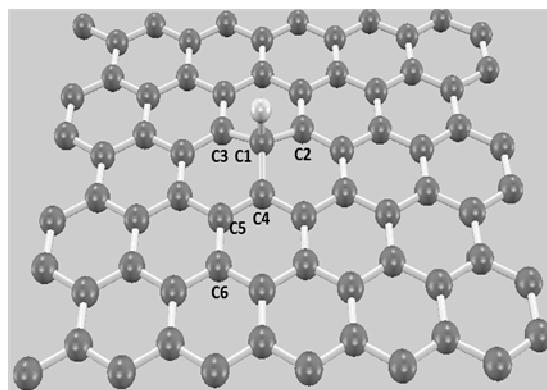


Fig. 1. Stable geometry of the mono-hydrogen on the graphene.

We performed nonmagnetic generalized gradient approximation (GGA) calculations of mono-hydrogen in graphene. The hydrogen atom is bonded to one carbon atom and the bond length between the two atoms is 1.14 Å. This bond length is close to that in a CH₄ molecule (1.09 Å), which is typical for sp³ C-H bonds. The position of the carbon atom bonded to the hydrogen

atom is 0.08 Å higher than the graphene plane (The first neighbor carbon atom is labeled as C_1 as shown in Fig.1). The bond angles between the first nearest carbon atom and the second nearest carbon atoms of C_2 , C_3 and C_4 in Fig.1 are 115.0°-115.1°. These values are between the sp^3 (109.5°) and sp^2 (120°) bond angles. The bond lengths between the first and second nearest carbon atoms is 1.49 Å, which is larger than the graphene bond length (1.42 Å) and shorter than the diamond bond length (1.54 Å). These results indicate that the character of the three bonds between the first and second neighbor carbon atoms is between those of sp^3 and sp^2 . The bond lengths of the C_4 - C_5 and C_5 - C_6 are 1.40 Å and 1.42 Å, and are close to the length that of graphene (1.42 Å). Therefore, except for the bonds between the first and second neighbor carbon atoms, the bond length in the graphene is close to that of the pristine graphene.

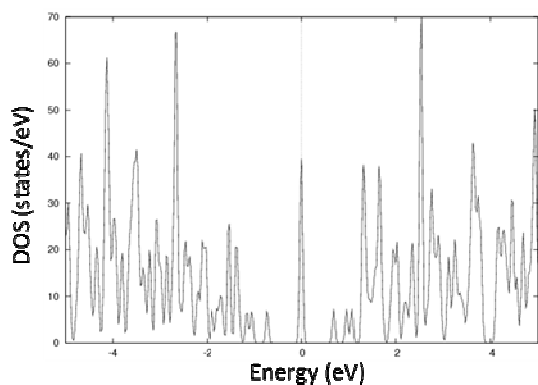


Fig. 2. The density of states of the nonmagnetic electronic structure of the mono-hydrogen on graphene. The energies are measured from the Fermi energy.

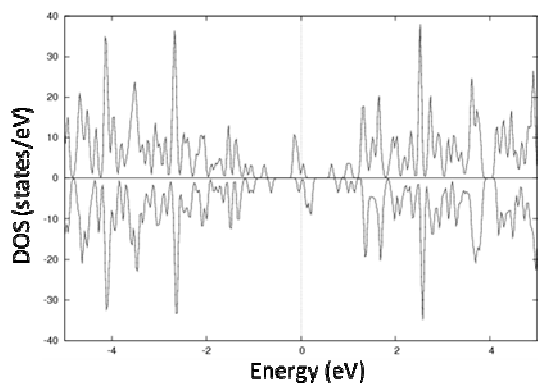


Fig. 3. The density of states of the spin-polarized electronic structure of the mono hydrogen on graphene. The energies are measured from the Fermi energy.

We next calculated the density of states (DOS). A sharp peak appears at the Fermi level (Fig.2). This result suggests that this electronic state is not so stable. Next, we carried out spin-polarized GGA calculations. We found that the energy is 80 meV lower than that of the nonmagnetic state. Previous studies also concluded that the spin-polarized state is the ground state [2-4]. As shown in Fig.3, peaks of the spin DOS of the majority spin and minority spin appear below and above the Fermi energy, respectively. The sharp peak in the

nonmagnetic state is split into two and the peak of the majority (minority) spin is occupied (unoccupied). This split of the peak is expected to be the reason why the spin-polarized state has lower energy than the nonmagnetic state.

We find that the bond lengths of the spin-polarized and nonmagnetic states differ only within 0.001 Å. Therefore, the geometry of the nonmagnetic state is very similar to that of the spin-polarized state.

We next show the spin density in Fig.4. The large spin density appears at hydrogen site and graphene. This result indicated that the hydrogen s-orbital is hybridized with the π orbital of graphene. The wavefunction in the graphene part has a nonbonding character and the amplitude is substantial only at B sub-lattices (Fig. 4b). It is thus expected that the part originates from the Dirac cone point.

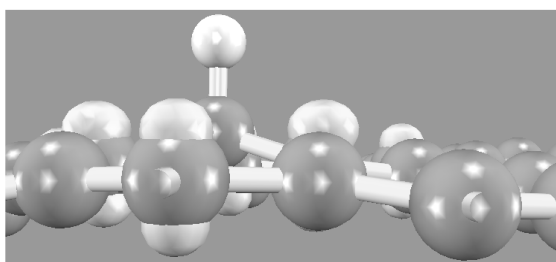


Fig. 4. Side view of the spin density of mono-hydrogen on graphene. The isosurface value is -0.01 (a.u)³.

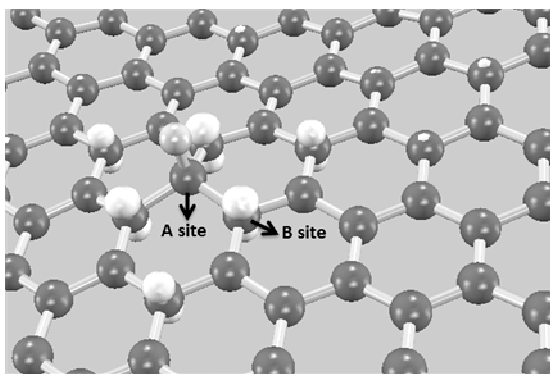


Fig. 5. Top view of the spin density of mono-hydrogen on graphene. The isosurface value is -0.01 (a.u)³.

3.2 Hydrogen mono-vacancy pair

We carried out calculations of a hydrogen-monovacancy pair (Fig. 6).

We find that the ground state is nonmagnetic. This result is consistent with a previously reported DFT based calculation [10]. In the most stable geometry, the hydrogen atom is bonded to the nearest carbon atom of the vacancy. The C-H bond length is 1.08 Å, which is shorter than that of the mono-hydrogen on graphene. The bond length of C_5 and C_9 (Fig.6) is found to be 1.88 Å. So there is a weak interaction between the two atoms. The bond length of C_1 - C_2 , C_2 - C_3 , C_3 - C_4 , C_4 - C_5 , C_5 - C_6 and C_6 - C_7 are 1.39 Å, 1.43 Å, 1.44 Å, 1.52 Å, 1.41 Å

and 1.41 Å, respectively.

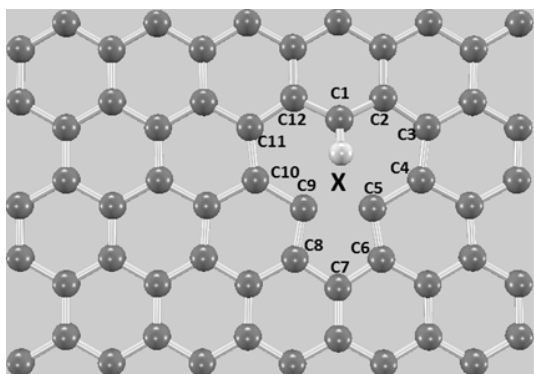


Fig. 6. Hydrogen mono-vacancy pair on the graphene

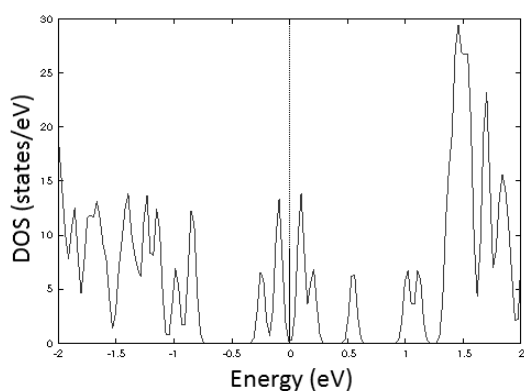


Fig. 7. Density of states for hydrogen mono-vacancy pair on the graphene. The energies are measured from the Fermi energy

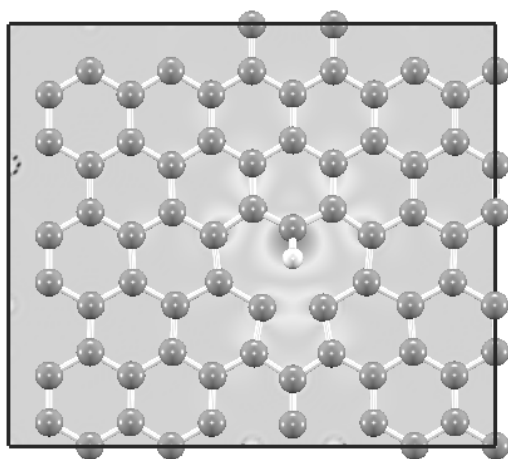


Fig. 8. Partial density of states for the energies ranging from -0.5 eV to 0.0 eV. The energies are measured from the Fermi energy (Fig. 7)

As shown in Fig.7, the density of states at Fermi level is almost zero. Therefore, the conductivity of the graphene is expected to be affected by this pair defect.

We calculated the electron density corresponding to the energies ranging from -0.5 eV to 0.0 eV in Fig. 7. As

Fig 8 shows, the electron distribution has a C-H bonding character. Since two electrons occupy the C-H bonding states, it is expected that there is a transfer of a single electron from the host graphene to this defect.

We considered the geometry where the hydrogen atom is bonded to carbon atom which is far (3.79 Å) from the vacant site. The energy of the nonmagnetic state is found to be 3.08 eV larger than that of the hydrogen mono-vacancy pair. By considering the spin-polarization that lower the total energy by 80 meV in the case of the mono-hydrogen in graphene, the dissociation energy is estimated to be 3.0 eV. The diffusion barriers of mono-hydrogen and mono-vacancy were estimated to be 0.98-1.2 eV and 1.7 eV, respectively [5-8]. Therefore, the barrier of mono-hydrogen is higher than that of mono-vacancy. Under the condition that mono-hydrogen is mobile, the pair is estimated to be formed since its dissociation energy is sufficiently high.

4. CONCLUSIONS

In conclusion, first principles study based on DFT was carried out to study the atomic structure of mono-hydrogen and hydrogen-vacancy pair on graphene.

Mono-hydrogen has a spin-polarized electronic structure. Its energy is 80 meV lower than that of the nonmagnetic state.

We also studied the hydrogen mono-vacancy pair. The dissociation energy of this pair into the mono-hydrogen in graphene and mono-vacancy is estimated to be large (3.0 eV). So, when the hydrogen diffuses in graphene, the pair is expected to be formed and this pair is nonmagnetic.

5. ACKNOWLEDGMENT

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