First-Principles Calculations of Adatom-Vacancy Pairs on the Graphene

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By using first-principles calculation, we study adatom-vacancy pairs on graphenes. We found that the healing barrier of the adatom-vacancy pair is very small (0.06 eV) when the adatom is bonded to a nearest carbon atom of the mono-vacancy. Therefore, this pair is easily healed. On the contrary, when the adatom is located 4.26-5.54 Å far from the vacant site, the healing barrier becomes high (0.24-0.32 eV), but these barriers are lower than that of the adatom diffusion. It is therefore expected that these adatom-vacancy pairs are healed in low temperature range where the adatom does not diffuse.

KEYWORD: first principle methods, graphene, adatom-vacancy pair, barrier

1. Introduction

Carbon nano-materials such as graphenes and nanotubes have attracted much attention since they are candidates for post-silicon device materials. Compared with conventional silicon devices, the effects of defects on carbon nano-device are expected to be serious because of the low dimensional conductivity. Therefore, the study of defects in sp^2 carbon systems is undertaken. Thus far, pentagon-hexagon pairs,[1] mono- and multi-vacancies,[2–8] adatoms,[9,10] adatom dimers,[11] and adatom-vacancy pairs[12] have been studied.

Among various defects, adatom related defects were observed at low temperatures. Recently low-energy electron irradiation on single-walled carbon nanotubes (SWCNTs) was performed.[14] The observation of *I*-*V* characteristic shows that some defects having some band gaps are created at low temperature by irradiation. Scanning tunneling microscope (STM) with the bias of 4.5 V at low temperature (95 K) also induces some unknown defects having band gaps.[15,16] These defects are expected to be related to adatoms which can be created by electron irradiation or STM. Meanwhile, a hydrogen thermal desorption spectroscopy showed that some defects in SWCNTs are healed at 44-70 K.[17] It was expected that the observed defect was the adatom-vacancy pair, so understanding of the stability

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and dynamical properties of the adatom-vacancy pair is necessary.

The purpose of this paper is to study the adatom-vacancy pair on the graphene by using first-principles calculations. We find that the healing barrier of the adatom-vacancy pair is very small (0.06 eV) when the adatom is bonded to a nearest carbon atom of the mono-vacancy. On the contrary, when the adatom is located 4.26-5.54 Å far from the vacant site, the healing barrier becomes high (0.24-0.32 eV). Therefore, the healing barriers depend on the position of the adatom.

2. Method

We use the spin-polarized generalized gradient approximation (GGA) within the density functional theory (DFT). Ultrasoft pseudopotential and plane wave basis set whose maximum kinetic energy is 25 Ry are used. In the optimized geometry of the graphite, the bond length is 1.42 Å, which is the same as the experimental value (1.42 Å). We use the 128-site supercell with the rectangle shape of the 17.04 $\times$ 19.68 Å^2 size. This size corresponds to the lattice constant of the pristine graphite. The sampling point in the two-dimensional Brillouin zone integration is 4.

We calculate the formation energy which is measured from the energy of the pristine structure, i.e., the formation energy is defined as the difference between the total energy of the defect system in the supercell and the multiplication of the energy of the perfect structure sheet per atom and the number of the atoms in the supercell.

In determining the diffusion barrier, we use the constrained optimization method.[18] First, we sample hyper-planes between initial and final geometries. Then we calculate the atomic force component which is parallel to each hyper-plane, and optimize the geometry on the hyper-planes. Among these optimized geometries, the geometry having the highest energy corresponds to the transition state.

3. Results and Discussion

3.1 The adatom bonded to a nearest atom of the vacancy site

We carry out calculations on the adatom-vacancy pair in graphenes (Fig. 1). We find that in the stable geometry, the adatom is bonded to a nearest atom of the vacancy. The calculated formation energy is 9.83 eV. Due to the relaxation, the distance between the two nearest atoms (C1 and C2 in Fig. 1) becomes small, and then the five member ring is formed (Fig. 1). The bond length between the two nearest atoms (C1 and C2) is found to be 1.85 Å, which is longer than the graphene bond length (1.42 Å). So the interaction between the two atoms is weak compared with that of the graphene bond. We here investigate the healing barrier of the adatom-vacancy pair. The position of the adatom in the transition state is slightly (0.05 Å) far from that in the stable structure of the adatom-vacancy pair. Since the transition state geometry is close to that of the stable adatom-vacancy pair, the healing

barrier energy is small (0.06 eV). Therefore, this defect can be healed at very low temperature. The barrier is much lower than that of the adatom diffusion barrier: The value was estimated to be 0.49 eV in our previous calculation.[18]

The recombination process of the interstitial and vacancy pair in the graphite[13] is similar to the healing one in the present system. However, the previously calculated barrier of the recombination (1.3 eV)[13] is much higher than that the healing barrier (0.06 eV) of the present system. This large barrier for the recombination is due to the fact that the interstitial atom in the stable geometry of the interstitial and vacancy pair is bonded to a nearest carbon atom of the vacancy and two carbon atoms which are located on the nearest graphite layer. In the recombination process, large energy is necessary to break these three bonds. On the other hand, in the present system, the adatom in the stable state is bonded to only a nearest carbon atom of the vacancy since the system consists of a single graphene layer. Therefore, the very low healing barrier of the present is expected to be intrinsic for the mono-layer graphene.

Previous first-principles studies were conducted for (9,0), (10,0), and (11,0) zigzag CNTs having adatom-vacancy pair defects.[12] It is found that the bond lengths in the five-member ring (corresponding to C1-C2 in Fig. 1) are 1.50, 1.52, and 1.54 Å for the (9,0), (10,0), and (11,0) nanotubes, respectively. These values are much smaller than the present value (1.85 Å) for the graphene. Since large energy is necessary to break these somewhat strong bonds, the healing barriers are expected to be large. Indeed, the calculated healing barriers were much larger than the present value for the graphene (0.06 eV): The barriers are 1.66, 1.98 and 2.14 eV for the (9,0), (10,0) and (11,0) nanotubes, respectively. The radii of these nanotubes are ~0.8 nm. Since the graphene corresponds to the CNT having the infinite radius, we expect that the healing barrier becomes low when the radii of the CNT become large.

3.2 The adatom bonded to an atom which is 4.26-5.54 Å far from the vacancy site

We study the case that the adatom is located a little bit far from the vacancy site. We choose several sites which are 4.26-5.54 Å far from the vacant site as shown in Fig. 2 and investigate the energetical stability of the geometries. The formation energies are 13.46, 13.20, 13.03, and 13.48 eV, for the B, C, D, and E geometries, respectively. These values are larger than the value of the A geometry where the adatom is bonded to a nearest atom of the vacancy (9.83 eV), which has been studied in the previous subsection. We expect that when the energy injected into the pristine graphene is somewhat larger than that induces the adatom-vacancy pair of geometry A, the defects of B-E are created. This energy injection is expected to be achieved by STM and electron irradiation experiments.[14–16]

Here, we study the healing barriers of C and D since their total energies are relatively small. First, we calculate the healing barriers of geometry C (Fig. 3(a)) and geometry D (Fig. 3(b)). It is found that

there are two transition states between geometry C and the perfect geometry as Fig. 3 shows. The first transition state (Fig. 3(c)) is located between geometry C and geometry D, where the energy of D is 0.17 eV lower than that of C. The energy of this transition state is 0.24 eV higher than that of geometry C. The second transition state (Fig. 3(d)) is located between geometry D (Fig. 3(b)) and the perfect geometry. The energy of this transition state is 0.23 eV higher than that of geometry D. Therefore, we conclude that the healing barrier of geometry C is 0.24 eV and that of geometry D is 0.23 eV.

We next study the healing barrier of geometry B (Fig. 4(a)). We find that the transition state (Fig. 4(b)) is located between geometry B and geometry A (Fig. 2). The energy difference between this transition state and geometry B is 0.32 eV. As was mentioned, the healing barrier of geometry A is very smaller (0.06 eV). Therefore, we conclude that the healing barrier of geometry B is 0.32 eV.

As mentioned above, when the adatom is located 4.26-5.54 Å far from the vacant site, the healing barriers are in the range of 0.24-0.32 eV. These values are much larger than that (0.06 eV) of geometry A where the adatom is bonded to a nearest carbon atom of the vacant site. Therefore, when the adatom is located somewhat far from the vacant site, the healing barrier becomes large. However, the healing barriers of geometries B, C, D are lower than the diffusion barrier of the isolated adatom (0.49 eV).[18] Therefore the defects having geometries B, C, and D are expected to be healed in the low temperature range where the adatom does not diffuse.

4. Conclusions

In this study we have investigated the adatom-vacancy pair in graphenes by carrying out first-principle calculations based on the spin-polarized GGA. We found that when the adatom is bonded to the nearest adatom of vacancy (geometry A), the healing barrier is very small (0.06 eV) and therefore this defect can be easily healed.

We have also performed calculations for the case that the adatom is located 4.26-5.54 Å far from the vacant site. The formation energies were found to be larger than that of geometry A. Therefore, we expect that these defects are created when the energy injected into the pristine graphene is somewhat larger than that induces the adatom-vacancy pair of geometry A. We find that the healing barriers are 0.24-0.32 eV. These values are larger than that of the geometry A but are smaller than that of the adatom diffusion barrier (0.49 eV).[18]

5. Acknowledgement

This work was partly supported by Grants-in-Aid for Scientific Research (Nos. 21560030 and 22016003) from the Japan Society for the Promotion of Science and by the RISS project in IT program of Ministry of Education, Culture, Sports, Science and Technology. The computations in this research

have been performed using the supercomputers at the ISSP, University of Tokyo, the RCCS, Okazaki National Institute, and the IMR, Tohoku University.

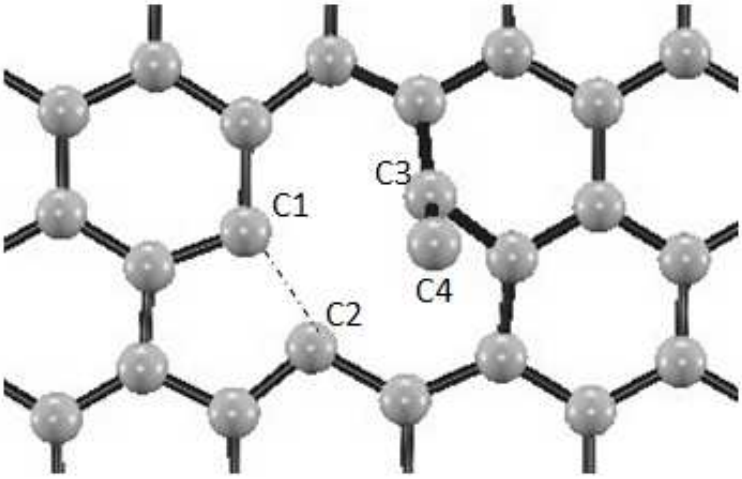

Fig. 1. Adatom-vacancy pair when the adatom is bonded to a nearest site of the vacancy in the graphene.

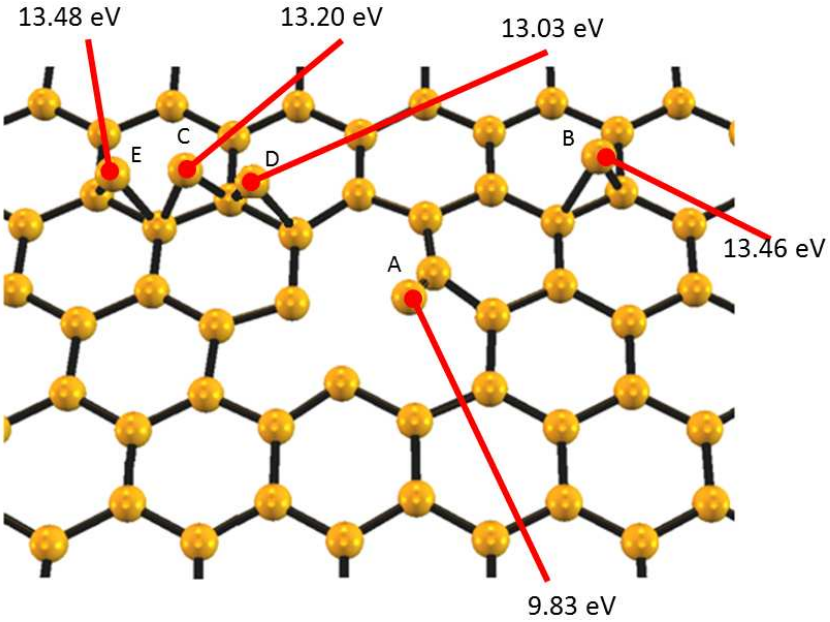

Fig. 2. (Color online)Formation energies of the adatom-vacancy pairs in the graphene.

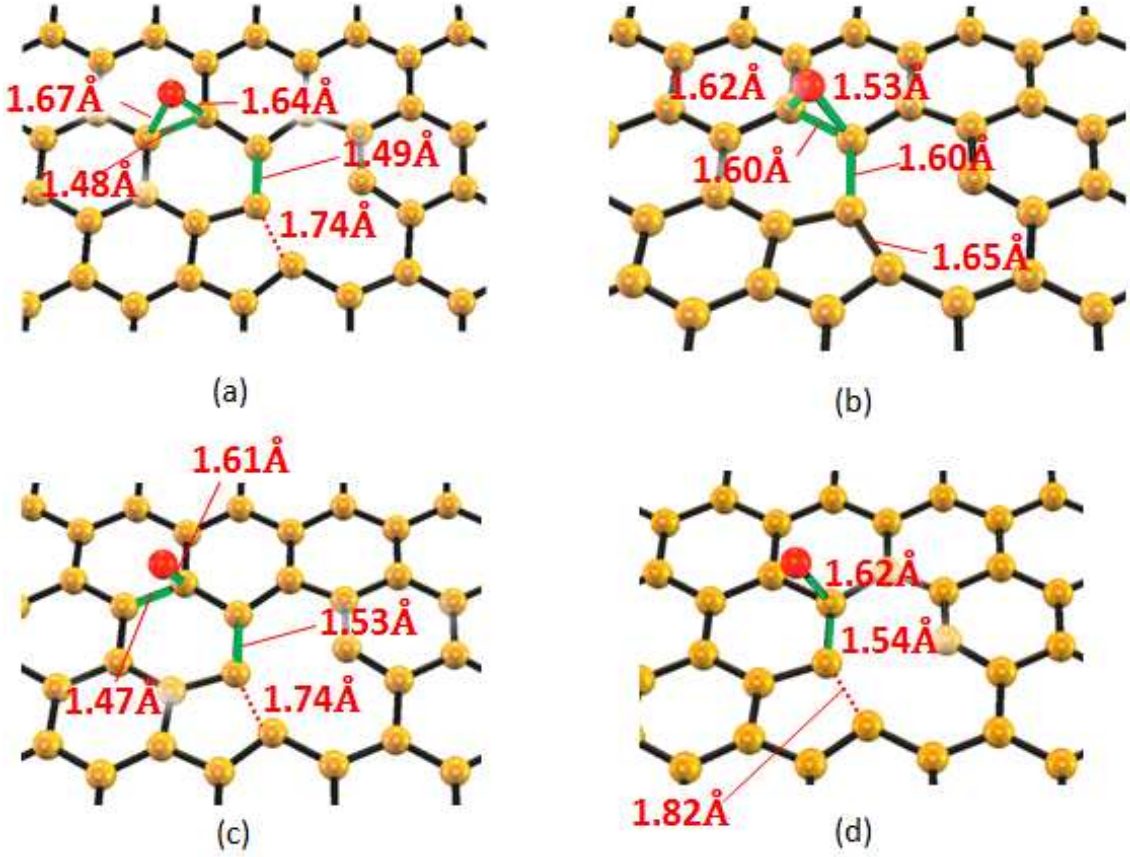

Fig. 3. (Color online)Healing path of geometry C and D. Geometry C and geometry D are shown in (a) and (c), respectively. Two transition states are shown in (b) and (d).

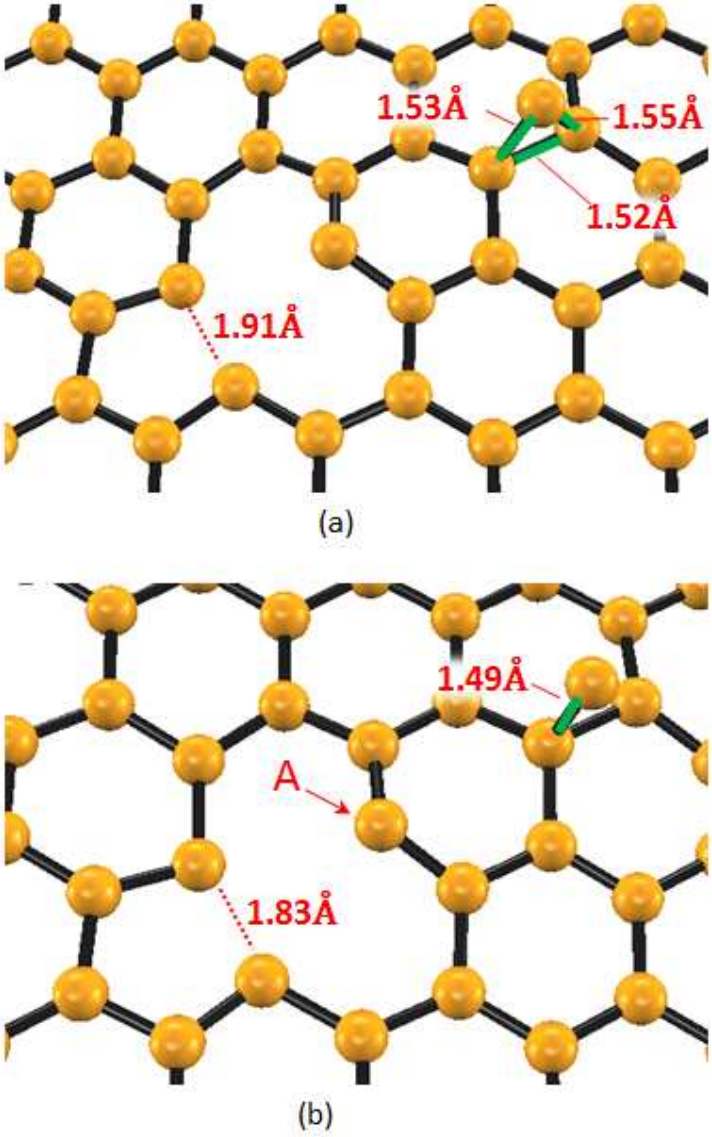

Fig. 4. (Color online)Adatom-vacancy pair when the atom little (5.54 Å) far from the vacancy in graphene (a) and the transition geometry (b).

References

1) A. J. Stone and D. J. Wales: Chem. Phys. Lett. **128** (1986) 501.
2) A. V. Krasheninnikov, K. Nordlund, M. Sirvio, E. Salonen, and J. Keinonen: Phys. Rev. B **63** (2001) 245405.
3) R. H. Telling, C. P. Ewels, A. A. El-Barbary, and M. I. Heggie: Nat. Mater. **2** (2003) 333.
4) A. A. El-Barbary, R. H. Telling, C. P. Ewels, M. I. Heggi, and P. R. Briddon: Phys. Rev. B **68** (2003) 144107.
5) A. V. Kransheninnikov, K. Nordlund, P. O. Lehtinen, A. S. Foster, A. Ayuela, and R. M. Nieminen: Phys. Rev. B **69** (2004) 73402.
6) C. P. Ewels, R. H. Telling, A. A. El-Barbary, M. I. Heggie, and P. R. Briddon: Phys. Rev. Lett. **91** (2003) 025505.
7) K. Yamashita, M. Saito, and T. Oda: Jpn. J. Appl. Phys. **45** (2006) 6534.
8) M. Saito, K. Yamashita, and T. Oda: Jpn. J. Appl. Phys. **46** (2007) L1185.
9) K. Nordlund, J. Keinonnen, and T. Mattila: Phys. Rev. Lett. **77** (1996) 699.
10) P. O. Lehtinen, A. S. Foster, A. Ayuela, A. Krasheninnikov, K. Nordlund, and R. M. Nieminen: Phys. Rev. Lett. **91** (2003) 17202.
11) M. Sternberg, L. A. Curtiss, D. M. Gruen, G. Kedziora, D. A. Horner, P. C. Redfern, and P. Zapol: Phys. Rev. Lett. **96** (2006) 075506.
12) S. Okada: Chem. Phys. Lett. **447** (2007) 263.
13) C. P. Ewels, R. H. Telling, A. A. El-Barbary, and M. I. Heggie: Phys. Rev. Lett. **91** (2003) 025505.
14) K. Kanzaki, S. Suzuki, H. Inokawa, Y. Ono, A. Vijayaraghavan, and Y. Kobayashi: J. Appl. Phys. **101** (2007) 034317.
15) K. Yamada, H. Sato, T. Komaguchi, Y. Mera, and K. Maeda: Appl. Phys. Lett. **94** (2009) 253103.
16) O. Tonomura, Y. Mera, A. Hida, Y. Nakamura, T.Meguro, K. Maeda: Appl. Phys. A **74** (2002) 311.
17) S.Arima, S.Lee, Y.Mera, S.Ogura, K.Fukutani, Y.Sato, K.Tohji and K.Maeda, Appl. Surf. Sci.**256**(2009) 1196-1199.
18) Y. Uramoto and M. Saito: J. Phys. Soc. Jpn. **79**, (2010) 074605.