Energetics and electronic structures of carbon nanotubes with adatom-vacancy defects

Susumu Okada [a,b,*]

[a] *Institute of Physics and Center for Computational Sciences, University of Tsukuba, Tsukuba 305-8571, Japan*

[b] *CREST, Japan Science Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

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Abstract

We report first-principle total-energy electronic-structure calculations in the density functional theory performed for carbon nanotubes with a defect consisting of a pair of an adatom and a vacancy. We find that the activation barriers for formation and healing of the defect are $\sim$ 10 and 2 eV, respectively, indicating the possibility of defect healing under moderate conditions. The defect is found to induce two gap states with characteristics that strongly depend on its arrangement. Further, the metal-insulator transition takes place on the (9,0) nanotube owing to the formation of gap states.

1 Introduction

Carbon nanotubes have attracted much attention in these years due to their structural and electronic properties that promise wide applications in nanometer-scale devices in the next generation [1–3]. One of their unique properties is that nanotubes are either metals or semiconductors depending on their atomic arrangements along the circumference [4,5]. This electronic property originates from the anisotropic energy bands of a graphite monolayer and a boundary condition imposed on the tubular structure. In addition to the chirality dependence of the electronic structure, the anisotropic energy band of the graphite monolayer also induces the characteristic modulation of their electronic properties by introducing imperfections [6–13]. Atomic imperfections in

* Corresponding author. FAX: +81-29-853-5924
Email address: sokada@comas.frsc.tsukuba.ac.jp (Susumu Okada).

the nanotubes are known to play a crucial role in determining their electronic properties near the Fermi level. Atomic defects (e.g. vacancies and interstitials) induce particular electron states at/near the energy gap [6–9]. Such states have been found to induce spin polarization around the defects [7,8] and modulation of ballistic conductance of nanotubes [6]. Furthermore, edges [10,11] and topological defects [12,13] results in the magnetic ordering on the nanotubes depending on the size and shape of the defects. These facts indicate that properties of nano-scale devices consisting of nanotubes are tunable by controlling their chirality as well as the defects on them. It is thus important to study the electronic properties of nanotubes with defects for their technological applications.

Recent reports show that single-walled carbon nanotubes are damaged by irradiation of electrons or photons with energies much lower than the threshold of the knock-on damage [14–16]. The defects are completely healed by annealing under moderate temperature [14,15]. Moreover, modulation of the electronic property, i.e. the metal-semiconductor transition, is found to take place on this damaging process [17,18]. These findings indicate that the modulation/recovery of intrinsic properties of nanotubes is possible in a controlled manner. Although experiments are elucidating the properties and formation conditions of the damaged nanotubes, only little is yet known on the fundamentals of these properties, especially on their geometries, energetics, and electronic structures. Thus, the purpose of the present work is to explore the atomic structure of the nanotubes damaged by electron/photon irradiation and to clarify their electronic structure and the energetics of damaging and healing processes of the defects.

2 Calculation methods

We perform total-energy electronic-structure calculations based on the density functional theory (DFT) [19,20]. To explore the possibility of polarization of the electron spin, the exchange-correlation energy of interacting electrons is treated in the local spin density approximation (LSDA) with a functional form [21] fitted to the Ceperley-Alder result [22]. The norm-conserving pseudopotentials generated by using the Troullier-Martins scheme are adopted to describe the electron-ion interaction [23,24]. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 50 Ry, which gives sufficient convergence of the relative total energies of carbon-related materials [23,25]. We adopt the conjugate-gradient minimization scheme both for the electronic-structure calculation and for the geometry optimization [26]. Structural optimization has been performed until the remaining forces for each atom are less than 5 mRy/Å. We also use the constraint minimization scheme to evaluate the activation barriers for damaging/healing processes of

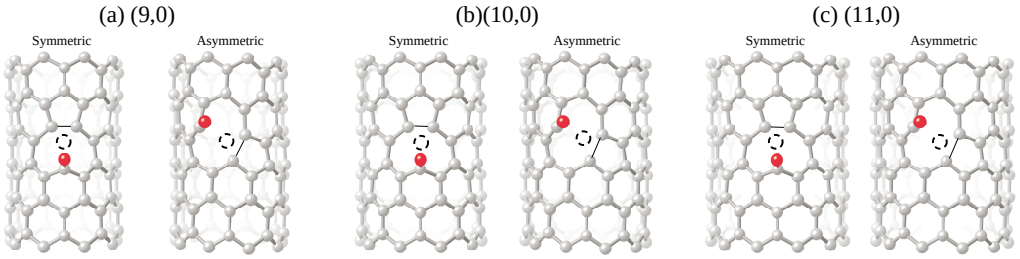

Fig. 1. (Color online) Optimized geometries of (a) (9,0), (b) (10,0), and (c) (11,0) nanotubes with a pair of an adatom and a vacancy. In each nanotube, left and right panels denote the symmetric and asymmetric arrangements of the defect, respectively. The red circle denotes the adatom which is diffused from the vacancy represented by the dashed circle. Thin solid lines denote the dimerized atoms under the structural optimization.

the nanotubes [27].

In the present study, we carry out the calculation on zigzag carbon nanotubes, $(n, 0)$ nanotubes, where $n = 9, 10, 11$, to study the diameter dependence of the electronic structure and energetics of damaged nanotubes. We adopt a supercell model, in which a nanotube is placed with its wall being separated by 7 Å from that of an adjacent one. To simulate the isolated defect on the nanotube, we consider the triple periodicity of a zigzag nanotube, which gives sufficient convergence of the electronic structure of the damaged nanotubes. Integration over one-dimensional Brillouin zone is carried out using the two k points ($k = \pm\frac{1}{4}$).

3 Results and discussion

3.1 Energetics

Figure 1 shows the optimized structures of zigzag nanotubes with a defect consisting of a pair of a vacancy and an adatom, in which the number of C atoms is identical to that of the pristine nanotubes. The structures are considered to be a possible candidate of the defects that have been observed in the experiments of the low-energy irradiation of electron/photon. For both symmetric and asymmetric cases, the nanotubes with an adatom-vacancy pair are found to be metastable in energy. In the optimized structures, the mono-vacancy is healed by a pentagonal ring as in the case of isolated mono-vacancy in nanotubes [7,8]. Owing to this structural relaxation, the adatom-vacancy pair is transformed into a pair of an adatom and a pentagonal ring.

We show the formation energy of the vacancy-adatom defect on the zigzag

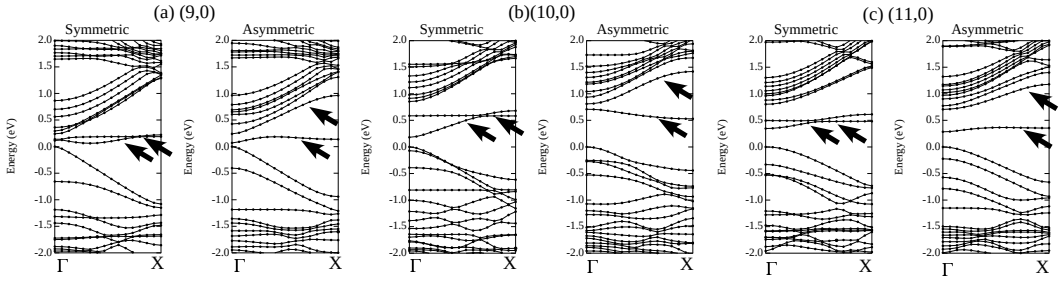

Fig. 2. Electronic structures of (a) (9,0), (b) (10,0), and (c) (11,0) nanotubes with a pair of an adatom and a vacancy. In each nanotube, left and right panels denote the symmetric and asymmetric arrangements of the defect, respectively. Energies are measured from the top of the valence band at the Γ points. Arrows indicate the gap states concerned with the defect formation.

Table 1
Formation energy (ΔE), activation barriers for damaging ($\Delta E_{\rm d}$) and healing ($\Delta E_{\rm h}$) of the adatom-vacancy defect.

		ΔE (eV)	$\Delta E_{\rm d}$ (eV)	$\Delta E_{\rm h}$ (eV)
(9,0)	Symmetric	8.09	9.75	1.66
	Asymmetric	8.59	10.83	2.24
(10,0)	Symmetric	8.46	10.46	1.98
	Asymmetric	9.79	11.05	1.26
(11,0)	Symmetric	8.66	10.80	2.14
	Asymmetric	9.98	11.56	1.58

nanotubes in Table 1. The formation energy of the defect depends on the diameter of the nanotubes: The energy increases monotonically with increasing tube diameter. Since nanotubes with small diameters are highly deformed from the ideal sp^2 hybridization, the atomic defect releases the large lattice strain around them resulting in the lower formation energy. The energy also depends on the direction of the bond associated with the protuberance atom. The formation energy for the asymmetric defect is higher than that for the symmetric one. The large formation energy of the asymmetric defect is ascribed to the weak dimerized character of the pentagonal ring. Indeed, the distances between the dimerized atoms for the symmetric defect are found to be 1.50, 1.52, and 1.54 Å for the (9,0), (10,0), and (11,0) nanotubes, respectively, indicating that the formation of the bond with substantial covalency. On the other hand, the distances for the asymmetric defect are 1.73, 1.75, and 1.82 Å for the (9,0), (10,0), and (11,0) nanotubes, respectively, which exceed those for the symmetric cases.

The activation barriers for damaging and healing of the defect are also listed in Table 1. The barriers for the damaging process are $\sim$ 10 and 11 eV for

symmetric and asymmetric defects, respectively. Thus, the adatom-vacancy defect with the symmetric arrangement easily takes place in comparison with the asymmetric defect. On the other hand, the barriers for the healing process are lower than those for the damaging process because of the large formation energy of the adatom-vacancy defect. The calculated barriers for the healing are $\sim 1 - 2$ eV. The results indicate that the adatom-vacancy defect is easily healed by thermal annealing under moderate temperature. Therefore, the adatom-vacancy defect is one of the possible candidates for the defect experimentally generated by the low-energy electron/photon irradiation on carbon nanotubes.

3.2 Electronic structures

Figure 2 shows the electronic structures of the nanotubes with an adatom-vacancy defect. The defect drastically modulates the electronic structure of pristine nanotubes: In a metallic (9,0) nanotube [Fig. 2 (a)], the metal-insulator transition takes place by introducing the defect. This modulation of the electronic properties has also been found in a previous experiment [17]. It is found that the energy gaps of the semiconducting nanotubes, the (10,0) [Fig. 2 (b)] and (11,0) [Fig. 2 (c)] nanotubes, are narrower than those in the pristine nanotubes. The modulation of electronic structures arises from the gap states induced by the adatom-vacancy defect: Two gap states emerge in all the nanotubes with the defect [28]. As for the symmetric defect, two deep levels with flat dispersion emerge in the lowest and the second lowest unoccupied states. The characteristics of the gap states slightly differ from the previous calculation, in which one of the two states is located near the conduction band edge exhibiting the shallow level character [9]. Curvature of nanotubes is one of possible origins for this different character of the gap states. The dispersion of these bands is so narrow that the electron transport in these states hardly takes place. Thus the symmetric adatom-vacancy defect induces the localized electron states which scatter the extended π-electron system on the carbon nanotubes.

In sharp contrast to the symmetric defect, one of two bands in the asymmetric defect lacks its dispersion, whereas the other shows substantial dispersion. In this case, the flat and dispersive bands correspond to the deep and shallow levels, respectively. Since the shallow level displays substantial dispersion, the tube with the asymmetric adatom-vacancy defect exhibits characteristic transport properties that are different from those on the nanotubes with a simple atomistic vacancy. Moreover, the carriers injected into the shallow level are expected to have substantial mobility.

We have analyzed the distribution of wave functions near the energy gap to

unravel the nature of the gap states. Figure 3 shows the isosurfaces of the wave functions of the gap states induced by a pair of an adatom and a vacancy. Two gap states in a symmetric defect are localized around the adatom. In sharp contrast, in the nanotube with an asymmetric defect the deep level is localized on the adatom with p character, while the shallow level exhibits a hybrid character between the p orbital on the adatom and the π states of the nanotube. This hybrid nature results from the substantial structural distortion of the nanotubes with an asymmetric defect. The distortion enables the p state

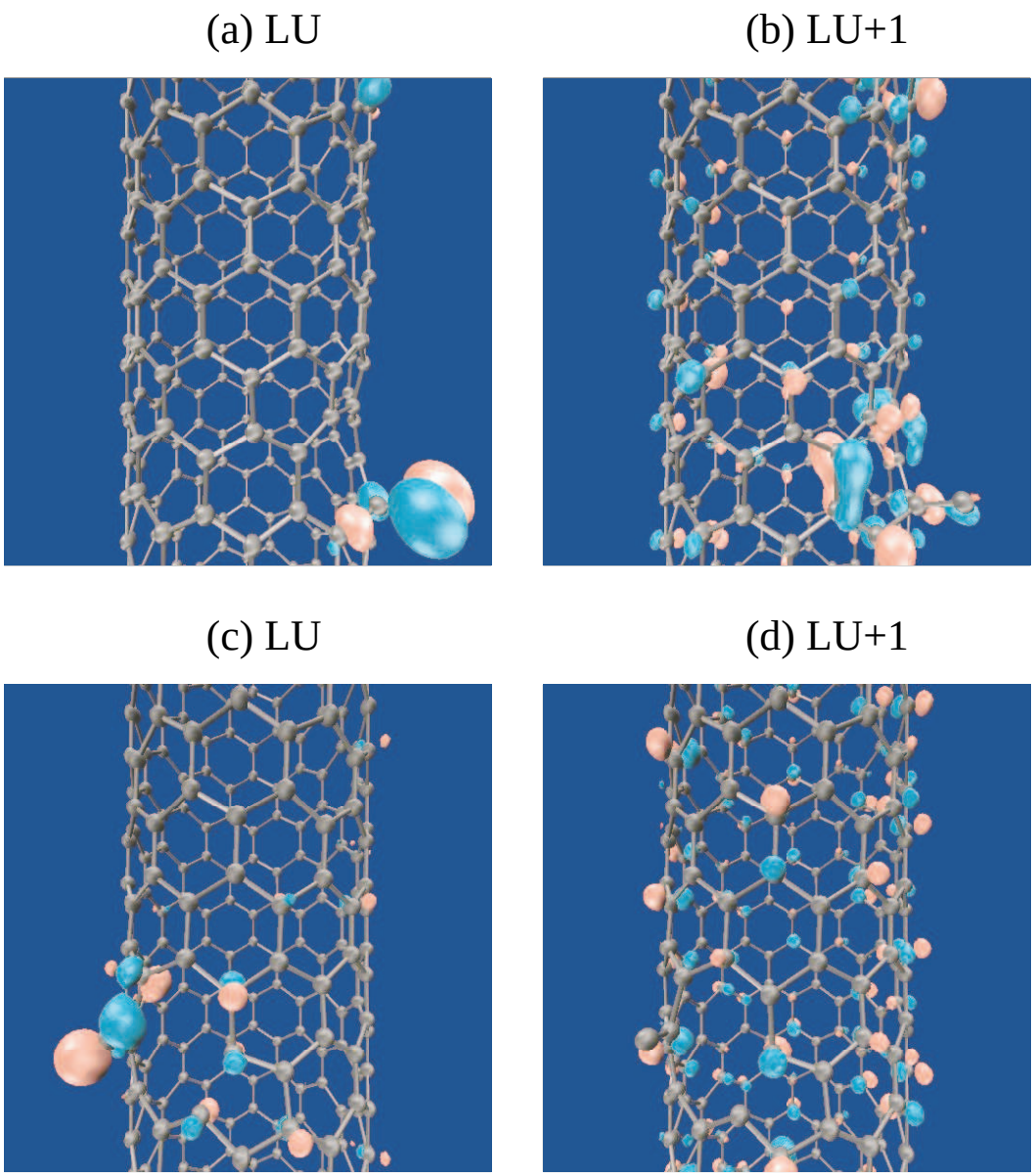

Fig. 3. Isosurfaces of the wave functions at the Γ point of the (11,0) nanotube with an adatom-vacancy defect. (a) The lowest unoccupied (LU) and (b) the second lowest unoccupied (LU+1) states for the symmetric defect and (c) LU and (b) LU+1 states for the asymmetric defect. Pink and cyan surfaces denote the positive and negative signs of the wave functions, respectively.

on the adatom to hybridize with the π states of the wall of the nanotubes. This result is also indicative of that nanotubes with an asymmetric adatom-vacancy defect exhibit remarkable transport properties via the shallow level generated by the defect.

4 Summary

We have studied the electronic structure and energetics of the carbon nanotubes with a defect consisting of a pair of an adatom and a monovacancy. Our calculations clearly indicate that the adatom-vacancy defect is a possible candidate for the defect on the carbon nanotubes generated by irradiation of low-energy electrons and photons: Activation barriers for damaging and healing of the nanotube calculated are $\sim$ 10 and 2 eV, respectively, depending on the arrangement of the defect on the nanotubes. The low activation barriers for the healing process can explain the experimental fact that the defects are easily healed by annealing under moderate conditions.

It is shown that the defect modulates the electronic structure of the nanotube. For a metallic nanotube, the defect opens an energy gap at the Γ point resulting in the metal-semiconductor transition. In addition to the metal-semiconductor transition, two gap states emerge in the newly generated energy gap. In semiconducting nanotubes, the defect also induces two gap states resulting in the narrowing of the fundamental gap of pristine nanotubes. These gap states possess the localized character around the defect with its symmetric arrangement. The asymmetric arrangement of the defect induces hybridization between the π states of the nanotube and one of two gap states with p character.

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References

[1] S.J. Tans, A.R.M. Verschueren, C. Dekker, Nature (London) 393 (1998) 49.

[2] R. Martel, T. Schmidt, H.R. Shea, T. Hartel, Ph. Avouris, Appl. Phys. Lett. 73 (1998) 2447.

[3] Y. Nosho, Y. Ohno, S. Kishimoto, T. Mizutani, Appl. Phys. Lett. 86 (2005) 073105.

[4] N. Hamada, S. Sawada, A. Oshiyama, Phys. Rev. Lett. 68 (1992) 1579.

[5] R. Saito, M. Fujita, M.S. Dresselhaus, G. Dresselhaus, Appl. Phys. Lett. 60 (1992) 2204.

[6] M. Igami, T. Nakanishi, T. Ando, J. Phys. Soc. Jpn. 68 (1999) 716.

[7] P.O. Lehtinen, A.S. Foster, Y. Ma, A.V. Krasheninnikov, R.M. Nieminen, Phys. Rev. Lett. 93 (2004) 187202.

[8] Y. Ma, P.O. Lehtinen, A.S. Foster, R.M. Nieminen, New J. Phys. 6 (2004) 68.

[9] S. Lee, G. Kim, H. Kim, B.-Y. Choi, J. Lee, B.W. Jeong, J. Ihm. Y. Kuk, S.-J. Kahng, Phys. Rev. Lett. 95 (2005) 166402.

[10] S. Okada, A. Oshiyama, J. Phys. Soc. Jpn. 72 (2003) 1510.

[11] S. Okada, A. Oshiyama, Phys. Rev. Lett. 87 (2003) 146803.

[12] S. Okada, K. Nakada, K. Kuwabara, K. Daigoku, T. Kawai, Phys. Rev. B 74 (2006) 121412(R).

[13] S. Okada, K. Nakada, T. Kawai, Appl. Phys. Lett. 90 (2007) 103120.

[14] S. Suzuki, K. Kanzaki, Y. Homma, S. Fukuba, Jpn. J. Appl. Phys. 43 (2004) L1118.

[15] S. Suzuki, Y. Kobayashi, Chem. Phys. Lett. 430 (2006) 370.

[16] S. Suzuki, Y. Kobayashi, J. Phys. Chem. C 111 (2007) 4524.

[17] S. Suzuki, Y. Kobayashi, Jpn. J. Appl. Phys. 44 (2005) L1498.

[18] K. Kanzaki, S. Suzuki, H. Inokawa, Y. Ono, A. Vijayaraghavan, Y. Kobayashi, J. Appl. Phys. 101 (2007) 034317.

[19] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864.

[20] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.

[21] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.

[22] D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. 45 (1980) 566.

[23] N. Troullier, J.L. Martins, Phys. Rev. B 43 (1991) 1993.

[24] L. Kleinman, D.M. Bylander, Phys. Rev. Lett. 48 (1982) 1425.

[25] S. Okada, S. Saito, A. Oshiyama, Phys. Rev. Lett. 86 (2001) 3835.

[26] O. Sugino, A. Oshiyama, Phys. Rev. Lett. 68 (1992) 1858.

[27] A. Ulitsky, R. Elber, J. Phys. Chem. 92 (1990) 1510.

[28] K. Iakoubovskii, N. Minami, Y. Kim, K. Miyashita, S. Kazaoui, B. Nalini Appl. Phys. Lett. 89 (2006) 173108.