

Chapter 4

ATOMIC STEPS ON THE NANOTUBE EDGE

We discuss the adsorption and the diffusion of the adatom on the flat NT edge and on the NT edge with several adatoms so far. The flat edge is not always guaranteed in the open edge growth of the NT. As well as a material surface, the atomic step is expected to be formed on the NT edge. A lot of efforts to clarify characteristics of the atomic step on the material surface has been performed. For example, the atomic step plays an important role in the epitaxial growth of the semiconductor [70, 71]. Therefore, we discuss here the atomic steps on the NT edge, that is, the single-row and double-row steps. In this chapter, both the LDA calculations and the TTB model calculations are performed. Within the TTB model, we considered a single-row step and a double-row step for the armchair edge and zigzag edge. The step formation energies are calculated for various radii. On the other hand, the LDA calculations are performed for the (8,8)-tube. The stable or metastable adsorption sites near the atomic step are explored by the LDA calculation. It is found that the site just below the step becomes a sink for the edge adatoms, indicating that the edge adatoms are likely to be adsorbed on this site. The flattening of steps is general a trend on the armchair edge.

4.1 Formation Energies and the Structures of Atomic Steps on the Nanotube Edge

Figure 4.1 shows structures of typical atomic steps at edges of NTs: (a) A single-row step of the armchair NT (S_A Step), (b) a double-row step of the armchair NT (D_A step), (c) a single-row step of the zigzag NT (S_Z step) and (d) a double-row step of the zigzag NT (D_Z step).¹ We calculate the step formation energy E_{step} for the S_A , D_A , S_Z and D_Z steps with various radii. Since the LDA calculation is formidable in the large radius nanotubes, we perform the TTB model calculation. We use a supercell model in which the NT is arranged periodically with a sufficiently large separation of 5.3 Å. The finite-length NT with stepped edge is placed at the centre of the

¹In this chapter, one zigzag line along the periphery of the zigzag NT is counted as one row.

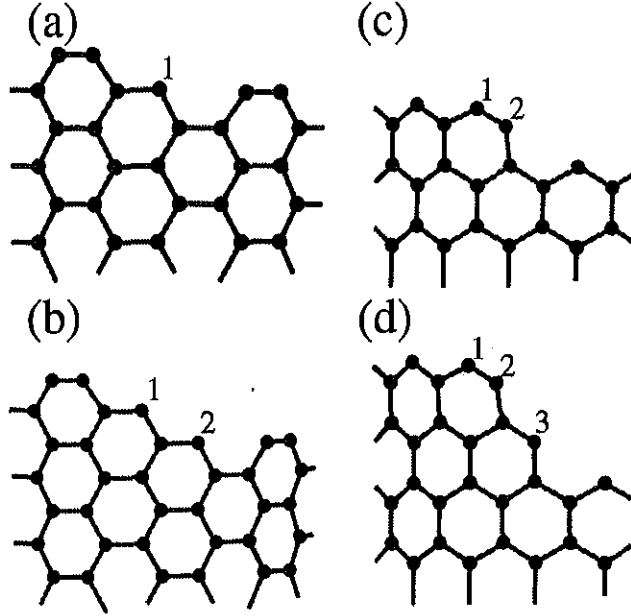


Figure 4.1: Side views of stepped edges of NTs. We depict only the region around the atomic step. (a) A single-row step of the armchair NT (S_A): The atom marked as 1 induces a DB. (b) A double-row step of the armchair NT (D_A): The atoms marked as 1 and 2 induce DBs. (c) A single-row step of the zigzag NT (S_Z). The atoms marked as 1 and 2 are connected by a triple bond. (d) A double-row step of the zigzag NT (D_Z). The atoms marked as 1 and 2 are connected by a triple bond. The atom marked as 3 in (d) induces a DB.

unitcell. This finite-length NT consists of $\sim 10^2$ carbon atoms. Each step is prepared on both edges of the finite-length NT and then the geometrical optimization is performed. Bond switching is not observed in any steps after the geometrical optimization. The step formation energies calculated by the TTB model are shown in Fig. 4.2. The formation energy is measured from the energy of the corresponding flat edge. In S_A step, a lonely atom marked as 1 (atom-1) in Fig. 4.1 (a) exists and is unable to be reconstructed. Hence, the formation of the DB at the atom-1 is the main source of the formation energy of the S_A step. Similarly in the D_A step, two lonely atoms substantially separated to each other exist (atom-1 and atom-2 in Fig. 4.1 (b)) and causes higher formation energy. It is found that the formation energy of the D_A step is indeed as nearly twice as that of the S_A step. Thus, it is concluded that the armchair edge prefers the flatness not to generate the DBs.

To investigate the structure of the atomic step on the armchair edge further, we perform the LDA calculations. We also use a supercell model. The finite-length (8,8)-tubes with the single-row stepped edge or double-row stepped edge are placed in the unitcell. This (8,8)-tube is arranged periodically with a sufficiently large separation of 5.3 Å. Each finite-length (8,8)-tube NT consists of 64 carbon atoms and the bottom atoms are hydrogenated. We perform the geometrical optimization for the stepped armchair edge then.

The geometrically optimized structures of the each atomic step are depicted in Fig. 4.3. In

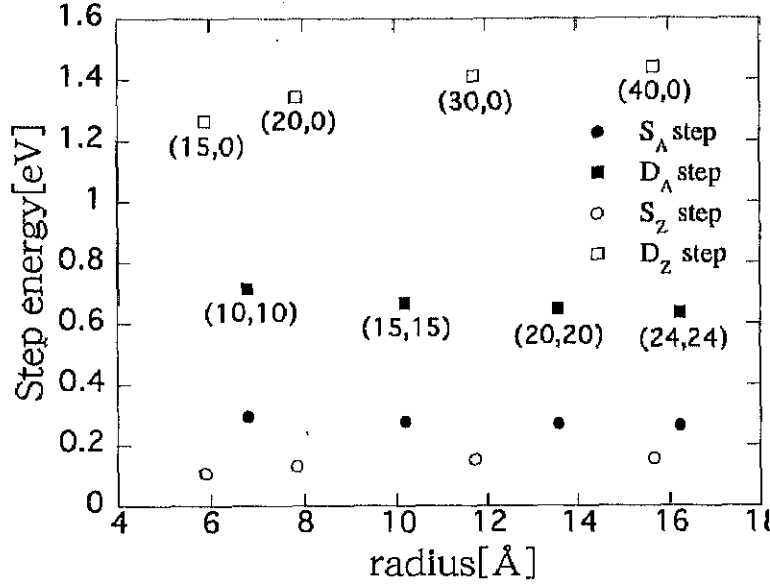


Figure 4.2: Step formation energies with respect to the finite length NT with the flat edges (TTB calculations). We pick up four kinds of NT each from armchair and zigzag type, that is, (10,10), (15,15), (20,20), (24,24), (15,0), (20,0) (30,0) and (40,0). Solid circles, solid squares, open circles and open squares indicate the formation energies of S_A step, D_A step, S_Z step and D_Z step, respectively.

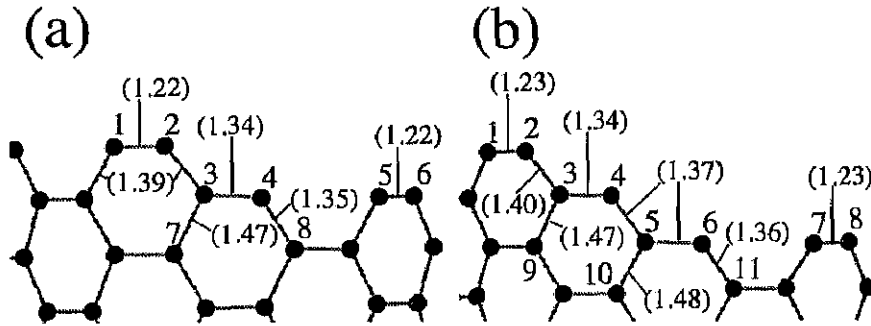


Figure 4.3: Side views of the geometrically optimized structures of the single- and double-stepped edge (LDA calculations). Only the region around the step is depicted. It is found that the region far from the step is not affected by the step. The bond lengths in Å are indicated in the parentheses. (a) The single step is depicted. The numbers of 1~8 are the atom indexes. The DB is generated on the atom marked as 4 (atom-4). The triple bonds are formed between the atom-1 and atom-2 and between the atom-5 and atom-6. The region from the atom-2 to the atom-8 is regarded as a tiny zigzag edge. (b) The double step is depicted. The numbers of 1~11 are the atom indexes. The DBs are generated on the atom-4 and the atom-6. The triple bonds are formed between the atom-1 and atom-2 and between the atom-7 and atom-8. The region from the atom-2 to the atom-11 is regarded as a tiny zigzag edge.

the case of the single step, the bond between the atom-1 and atom-2 (The C_1-C_2 bond. The " C_i-C_j " bond indicates a bond between the atom- i and atom- j .) and the C_5-C_6 bond in Fig. 4.3 (a) become the triple bond. The DB is generated on the atom-4. Because this DB interacts with the electrons of the atom-3 and atom-4, the C_3-C_4 bond (C_4-C_8 bond) is shortened to be 1.34 Å (1.35 Å). The C_3-C_7 bond is weakened instead and the bond length becomes 1.47 Å. This effect of the DB on the step is similar to the case of the flat zigzag edge. In fact, we can regard the region from the atom-2 to the atom-8 in Fig. 4.3 (a) as a tiny zigzag edge. In the case of the double step, the C_1-C_2 bond and the C_7-C_8 bond is triple bond. It is found that the triple bond formation is not affected by the step (See Fig. 4.3 (b)). Similar to the single step, the region from the atom-2 to the atom-11 can be regard as a tiny zigzag edge. The DBs are generated on the atom-4 and atom-6 with the result that the C_3-C_4 , C_4-C_5 , C_5-C_6 and C_6-C_{11} bonds are shortened to be 1.34~1.37 Å and the C_3-C_9 bond (C_5-C_1 bond) is weakened and the bond length becomes 1.47 Å (1.48 Å).

It is found that the atomic step on the armchair edge introduces a tiny region of the zigzag edge and generates the DB. The higher the atomic step becomes, the more the DB is generated on the tiny zigzag edge region by the step formation.

In the case of the stepped zigzag edge, the atoms near the S_Z step (atom-1 and atom-2 in Fig. 4.1 (c)) interact with each other and hereby form a triple bond: The bond length between the atom-1 and atom-2 in Fig. 4.1 (c) obtained by the TTB calculations is ~ 1.2 Å. Since the formation of a triple bond gains an energy substantially, the formation energy of the S_Z step is relatively low. We have considered that the hexagon networks are formed successively on the edge (the series of the hexagons) during the open edge growth of the zigzag NT. When the series of the hexagons are formed on the zigzag edge, the S_Z step is constructed. The successively formation of the hexagons along the zigzag edge corresponds to the step flow growth of the NT. The relatively low formation energies of the S_Z step indicate a probability of the step flow growth of the zigzag NT. On the other hand, the D_Z step also has a triple bond between the atom-1 and atom-2 in Fig. 4.1 (d). Yet a lonely atom-3 exists in the D_Z step and a DB is hereby generated. Furthermore, the D_Z step is accompanied by substantial lattice distortion near the edge. As a result, the high activation energy is required to form the D_Z step. It is found that the D_Z step is hardly formed on the zigzag edge.

4.2 Adsorption near the Single-Row Step and Double-Row Step

The adatom adsorption near the armchair single-row step is investigated by the LDA calculations. The finite (8,8)-tubes with step given in the previous section is also used here. We explore the stable or metastable adsorption sites near the single-row step at first. Five stable or metastable adsorption sites are obtained as shown in Fig. 4.4 (a). At each site, the adsorption energies of the single adatom are calculated. The adsorption energies of each adsorption site are summarized in Table 4.1. At all adsorption sites we consider, it is found that the adatom is always double-

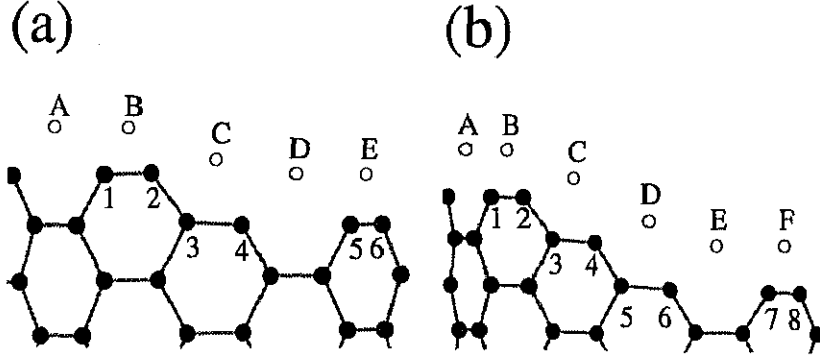


Figure 4.4: The adsorption sites near the step on the armchair NT are indicated by the open circles. (a) The single-row step on the armchair: We calculate the adsorption energies of the single adatom on the 5 adsorption sites ($A \sim E$). A : the seat site above the step. B : the arm site above the step. C : the site just above the tiny zigzag edge region. D : the seat site below the step. E : the arm site below the step. The numbers of 1 ~ 6 are the atom indexes. The DB is generated on the atom marked as 4 (atom-4). The bonds between atom-1 and atom-2 and between the atom-5 and atom-6 are the triple bond. (b) The double-row step on the armchair: We calculate the adsorption energies of the single adatom on the 6 adsorption sites ($A \sim F$). A : the seat site above the step. B : the arm site above the step. C and D : the site just above the tiny zigzag edge region. E : the seat site below the step. F : the arm site below the step. The numbers of 1 ~ 8 are the atom indexes. The DBs are generated on the atom-4 and atom-6. The bonds between atom-1 and atom-2 and between the atom-7 and atom-8 are the triple bonds.

Table 4.1: Adsorption energy E_{ad} of the adatom near the armchair single-row step and double-row step.

Site	$E_{\text{ad}}(\text{single step})$ [eV]	$E_{\text{ad}}(\text{double step})$ [eV]
A	7.83	7.63
B	8.58	8.42
C	8.25	7.95
D	9.42	8.51
E	8.45	9.24
F	-	8.31

coordinated. The A (D)-site is the seat site above (below) the step and the pentagon network is formed by the adatom adsorption. The adatom adsorption at the A -site is similar to the case of the flat armchair edge. The adatom generates the two DBs on the atom-2 and the opposite seat site. On the other hand, the adatom on the D -site generates the DB on the atom-6 and eliminates the DB originally generated on the atom-4 by the step formation. Except for the DB on the adatom itself, while the adatom on the A -site generates the two DBs, the adatom on the D -site does not increase the number of DB on the edge. Therefore, the adsorption energy of the D -site is 1.59 eV larger than that of the adsorption on the A -site. It is found that the adsorption on the seat site below the step is more stable than those of the seat site above the step and the seat site of the flat armchair edge, since the DB generated by the step formation is eliminated.

The C -site is just above the tiny zigzag edge region generated by the step formation. The adatom on the C -site is bonded to the atom-2 and atom-4 with the result that the square network is formed. This adatom also eliminates the DB on the atom-4. The lengths of the bond between the adatom and the atom-2 (The C_a-C_2 bond. The subscript "a" indicates the "adatom".) and the C_a-C_4 bond are 1.51 Å and 1.41 Å, respectively. (In the case of the flat (9,0)-edge, the adatom which forms the square network is bonded to the edge atoms with length of 1.45 Å. See Fig. 3.4.) It is indicated that the adatom is bonded more strongly to the atom-4. The C_1-C_2 bond is weakened by the adatom adsorption on the C -site and the bond length becomes 1.27 Å. Although both the adatom on the C -site and D -site eliminate the DB on the atom-4, the adsorption energy of the D -site is larger than that of the C -site. This is because the local distortion induced by the square network is larger than that induced by the pentagon network. The B (E)-site is the arm site above (below) the step. It is found that the adatoms on both the arm sites above and below the step form the triangle networks and the adsorption energies of B -site and E -site are almost same. In the case of the single-row step, it is concluded that the seat-site below the step becomes the most stable site for the adatom. This is the effect of the DB originally generated on the atom-4. In other words, the single step formation on the armchair edge yields only this DB. Therefore, only the adsorptions on the C -site and D -site are affected by the step through the DB on the atom-4. It is expected that the effect of the step on the adsorptions on the A -site, B -site and E -site is substantially small.

The discussion of the double-row stepped armchair edge is similar to the case of the single-row stepped edge. The two DBs are generated on the atom-4 and atom-6 by the step formation. We also explore the stable or metastable adsorption sites near the double step and find 6 stable or metastable sites as shown in Fig. 4.4 (b). Two metastable adsorption sites on the tiny zigzag edge region are obtained. At all these adsorption sites, it is found that the adatom is always double-coordinated. The adsorption energies obtained by the LDA calculations are summarized in Table 4.1. The A (E)-site is the seat site above (below) the step. The adatom on the A -site forms the pentagon network and two DBs are generated. On the other hand, the adatom on the E -site also forms the pentagon network and generates the DB on the atom-8 and eliminates the DB on

the atom-6. Therefore, the adsorption energy of the *E*-site is larger than that of the *A*-site as well as the case of the single step. The *B* (*F*)-site is the arm site above (below) the step. For both cases, it is found that the adatom forms the triangle network and weakens the triple bond beneath the adatom. The difference of the adsorption energy between the *B*-site and *F*-site is also small. The *C*-site and *D*-site are adsorption sites above the tiny zigzag edge region. The adatom on the *C*-site is bonded to the atom-2 and atom-4 with lengths of 1.53 Å and 1.40 Å, respectively, with the result that the square network is formed. It is found that the C_1-C_2 bond is weakened by the adsorption and the bond length becomes 1.27 Å. While the adatom on the *C*-site eliminates the DB and weakens the triple bond (C_1-C_2 bond), the adatom on the *D*-site eliminates the two DBs on the atom-4 and the atom-6. Therefore, the adsorption energy of the *D*-site is larger than that of the *C*-site. It is found that the adatoms each on the *C*-site, *D*-site and *E*-site eliminate the DBs generated by the step formation. Among these three sites, the *E*-site becomes the most stable adsorption site, since the square network on the tiny zigzag edge region formed by the adsorptions on the *C*-site or *D*-site induces the local lattice distortion. In the both case of the single-row and double-row stepped armchair edge, it is concluded that the seat site below the step is the most stable adsorption site. Even the adsorption energy of the *D*-site of the double step where the two DBs are eliminated is less than that of the seat site below the step. This result suggests that, in the case of the step which is higher than the double step, the seat site below the step also becomes the most stable adsorption site. The edge adatom is likely to be adsorbed on the seat site below the step and the pentagon network is formed.

We calculated here only the adsorption energy on the stable (metastable) sites near the step. The activation energy of diffusion near the step is not investigated. When the adatom diffuses along the single-row or double-row stepped edge, it is expected that the adatom is one- or two-coordinated. This coordination number is same as the case of the diffusion on the flat armchair edge. This fact is quite different from the diffusion near the step of the usual material surface, for example, the step of the Si (100) surface. In the case of the diffusion near the step of material surface, the coordination number of the adatom at the step edge usually becomes less than that of the adatom on the flat surface, because of missing of the top-row atoms to which the adatom is bonded at the step edge [70]. The adsorption energy is decreased as a result of the decrease in the coordination number of the adatom. In other words, the activation energy to diffuse beyond the step becomes large. On the contrary, the coordination number is increased at the site just below the step with the result that the adsorption energy is increased. The site just below the step becomes a sink for the diffusing adatom on the stepped material surface. On the other hand, the coordination number of the adatom diffusing on the stepped armchair NT edge is not increased at the site just below the step and not decreased at the site just above the step as compared with the adatom on the flat edge. The increase in the adsorption energy caused by the increase in the coordination number is not expected for the stepped NT edge. However, in the case of the stepped armchair edge, the site just below the step is the sink for the adatom. This is due to

the DB previously generated at the site below the step by the step formation. Furthermore, it is also expected that the activation energy of the diffusion is not substantially modified by the step, because the variation of the coordination number of the adatom diffusing through the step is same as the case of the diffusion on the flat NT edge. Although the adatom diffusing on the stepped armchair edge is always one- or two-coordinated, the adatom diffuses on two kind of the edges, that is, *armchair edge* \rightarrow *zigzag edge* \rightarrow *armchair edge*. We have concluded in chapter 3 that the activation energy of the diffusion on the flat zigzag edge is less than that of the diffusion on the flat armchair edge. Therefore, it is expected that the edge adatom diffuses on the step of the armchair edge more easily than the diffusion on the flat armchair edge.

4.3 Summary

The energetics of the atomic steps on the NT edge and the adatom adsorption near the step structure are investigated. Generally speaking, the higher the step is, the larger the step formation energy is. For the atomic step on the armchair edge, the tiny zigzag edge is formed at the step with the result that the DB is generated. This DB generation is main source of the step formation energy. On the other hand, in the case of the S_z step, the relatively low formation energy suggest that a probability of the step flow growth of the zigzag NT. We also explore the stable or metastable sites near the single- and double-row step on the armchair edge. For both steps, it is concluded that the seat site below the step is the most stable site for the edge adatom. This is due to the elimination of the DB generated by the step formation.