

Investigation of the Nitrogen Effect on the Carbon Nanotube Growth by Ab-initio Calculation

Hyo-Shin Ahn^{1,2}, Tae-Young Kim¹, Seung-Cheol Lee¹, Kwang-Ryeol Lee^{1,*} and Doh-Yeon Kim²

¹Future technology research division, Korea Institute of Science and Technology, Seoul 136-791, Korea
Fax: 82-02-958-5509, e-mail: krlee@kist.re.kr

²School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

We investigated the effect of nitrogen incorporation on the carbon nanotube (CNT) growth by ab-initio calculation. Two possible effects of nitrogen incorporation were tested in the present work: the reduction of the strain energy for tubular graphite sheet or the reduction of the kinetic barrier for the CNT growth. The strain energy of tubular form of graphite decreased as the diameter of CNT increased. The strain energy becomes negligible when the diameter of CNT was larger than 35 Å. Hence, the effect of nitrogen incorporation to reduce the strain energy of tubular graphite is not significant in most cases of the CNT growth. In order to estimate the kinetic barrier for CNT growth, transition state calculations were carried out for every step of carbon attachment. The kinetic barrier for carbon attachment without nitrogen was estimated to be 176 meV for zigzag growth edge or 160 meV for armchair edge. However, the nitrogen incorporation significantly reduced the kinetic barriers in a certain configuration. Especially, when nitrogen is located on the top edge of zigzag growth front, the kinetic barrier disappeared. Enhanced growth of CNT by nitrogen incorporation was discussed in terms of the reduction of the kinetic barrier.

Key words: Vertically aligned carbon nanotube, Growth kinetics, Nitrogen effect, Ab initio calculation, strain energy

1. INTRODUCTION

Vertically aligned carbon nanotube (VACNT) has been considered as one of the strong candidates for various industrial applications ranging from flat panel display to energy storage materials [1, 2]. In most deposition condition, nitrogen environment in the growth stage was necessary to evolve the vertically aligned carbon nanotube (VACNT) growth [3-5]. Recently, present authors investigated the effect of the growth environment on the CNT growth [5]. We showed that the nitrogen incorporation to the CNT wall or cap enhances the growth rate of the CNTs, which results in the vertical alignment during growth. The nitrogen incorporation to CNT is enhanced when the activated nitrogen exists in the growth environment. In thermal CVD condition, the VACNT growth occurs only when using NH₃ environment since only NH₃ can be decomposed to generate the activated nitrogen [5].

Even if the previous work definitely showed an intimate relationship between the CNT growth rate and the nitrogen incorporation, the role of nitrogen on the CNT growth is yet to be understood. In the present work, the role of nitrogen in the CNT growth was investigated by ab-initio calculation using Dmol³ [6] with generalized gradient approximation (GGA) [7, 8]. Two possible roles were tested in the present work: first, nitrogen incorporation would reduce the strain energy for bending graphite sheet to tubular form. Typical diameter of the VACNTs ranged from 300 to 400 Å [5]. In order to calculate the effect of the strain energy of CNT with diameter larger than 10nm, we employed a cluster design method [9]. The other possible role is to reduce the kinetic barrier for carbon atom attachment on the growth front of the CNTs. Transition state

calculations were carried out on each step of the growth. The present calculation shows that the strain energy of the tubular graphite is negligible when the diameter is larger than 35 Å, while the nitrogen incorporation reduced the kinetic barrier in a certain configuration. Especially, when nitrogen is located on the growth edge, the kinetic barrier for the growth can be reduced to zero, depending on the position of the incorporated nitrogen.

2. CURVATURE EFFECT OF CARBON NANOTUBE ON STRAIN ENERGY

Carbon nanotube is essentially a tubular form of graphite constructed by rolling-up a graphite sheet. Due to its curvature, carbon nanotube has excess strain energy with respect to the graphite sheet. The strain energy would be a function of the curvature of the CNT wall, which is known to be inversely proportional to the square of the radius [10]. Total energy calculations for various curvatures of the CNT structure have been carried out and showed a good correspondence with the theoretical predictions [11, 12]. However, the previous calculations were limited in diameter up to 1 nm due to the limited computing power. In order to overcome the limitation, we adapted a cluster design calculation [9]. By the cluster design calculation, we examined the energies of CNTs with the radii from 4Å to 200Å.

Fig. 1 shows the relationship between the calculated excess strain energy and the radius of CNT wall. Calculated data agreed well with the theoretical relationship between the strain energy and the radius of graphite sheet, $\Delta E \propto 1/R^2$ [10]. As the radius increased, the excess strain energy of CNT decreased down to zero. The calculation shows that the critical radius of CNT

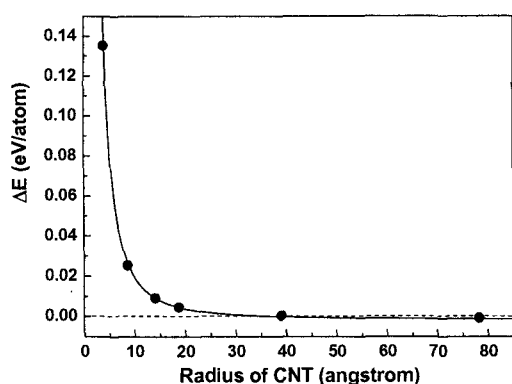


Fig. 1. Dependence of the excess strain energy (ΔE) on the radius of CNT.

where the excess strain energy becomes zero is 35 Å. Consequently, CNTs of radii larger than 35 Å do not have the excess strain energy. Since the typical radius of the vertically aligned carbon nanotube ranged in 150–200 Å, the CNTs can be considered as a strain free structure. Hence, the role of nitrogen incorporation to reduce the strain energy can be excluded.

3. GROWTH KINETICS OF CARBON NANOTUBE

3.1 Growth of Pure Carbon Nanotubes

In the present work, the role of catalyst was reasonably assumed to assist the formation of the growth precursor of carbon and provide the easy diffusion path to the growth front for the carbon atoms. Based on the result in the previous section that the strain energy is negligible in the CNTs of diameter larger than 35 Å, we also assumed that the growth kinetics of the flat graphite sheet is associated with that of the CNT of large diameter. For the kinetics calculation, we designed a simple structure of the growth front in the carbon nanotube wall. According to the symmetry of hexagon network, there are two kinds of the front edge: zigzag and armchair edge as shown in Fig. 2 (a). Because any growth front of the CNT can be expressed in terms of the mixture of these two front edges, it would be valuable to consider the growth kinetics in these two extreme cases.

Fig. 2 (b) shows the sequence of the atom attachment on each front edge. On armchair edge, another hexagon ring requires two more carbon atoms, where two reaction steps are involved. The first atom forms a pentagon ring on the front edge followed by the second atom attachment to make a hexagon ring. On the zigzag edge, three carbon atoms are needed to form another hexagon ring. Three reaction steps to form tetragon, pentagon and hexagon ring formation.

Kinetic barrier for each reaction step was calculated by the transition state calculation. All the structures were relaxed during calculation. Fig. 3 shows the kinetic barriers for the reactions steps. On the zigzag edge, both the tetragon formation and the transition from pentagon to hexagon occur spontaneously without any kinetic barrier. However, the transition from tetragon to pentagon has a kinetic barrier of 176 meV. On the armchair edge, pentagon formation has a kinetic barrier of 160 meV, and the transition from pentagon to hexagon

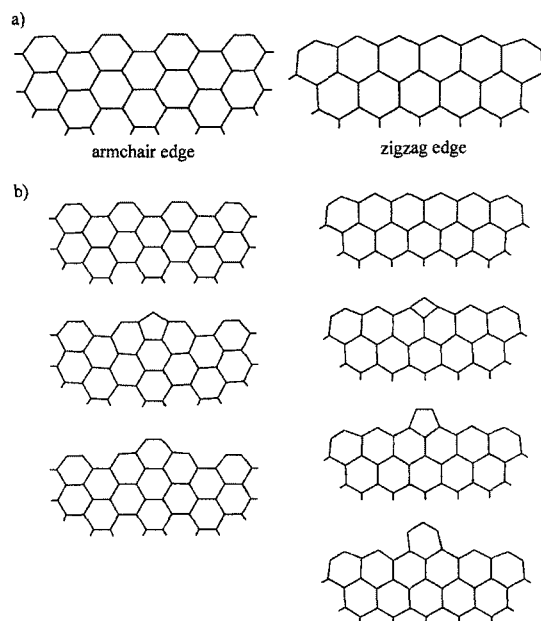


Fig. 2. (a) Two structures of growth front; armchair and zigzag edge. (b) Schematics of the growth sequence of each edge.

also has a kinetic barrier of 64 meV. It can be thus expected that the growth kinetics on the armchair edge is much faster than those on the zigzag edge. However, because the growth on the armchair edge eventually results in the zigzag edge, the total growth kinetics would be determined by the growth kinetics on the zigzag edge.

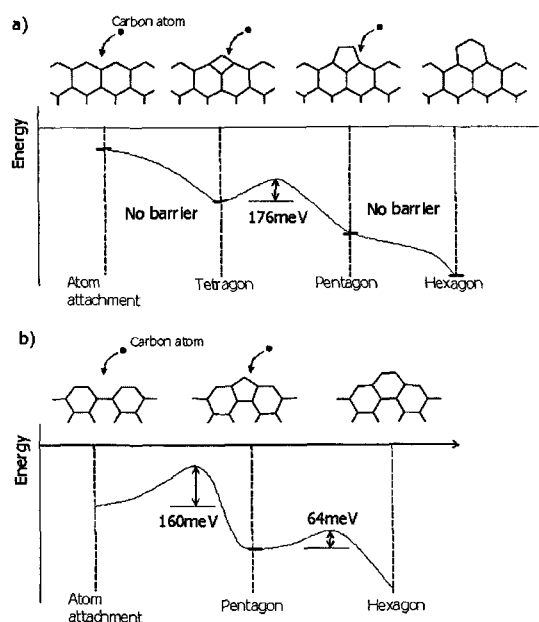


Fig. 3. The sequences of the growth and the energy diagram for each reaction step on a) zigzag edge and b) armchair edge in pure carbon system.

3.2. Growth of CNT with Nitrogen

3.2.1 Nitrogen Incorporation

Considering carbon nanotube growth with nitrogen, we first examined the nitrogen incorporation into pure carbon hexagonal network. Nitrogen can be involved in any step of the growth. Fig. 4 schematically shows the nitrogen incorporation on the armchair edge. Nitrogen can be introduced at the step of pentagon-hexagon transition (Fig. 4 (a)) or at the step of pentagon formation (Fig. 4 (b)) followed by carbon attachment.

In the former case shown in Fig. 4 (a), pentagon formation is the same reaction of pure carbon nanotube growth. Then, nitrogen is attached and makes an additional hexagon ring, of which kinetic barrier was 137 meV. In the latter case shown in Fig. 4 (b), pentagon formation with nitrogen has a kinetic barrier of 303 meV, and the following carbon attachment also has a very high kinetic barrier (5455 meV). Since the reaction paths are mutually exclusive, the former reaction would be preferred. However, it must be noted that the nitrogen incorporation in the stage of pentagon-hexagon transition has higher kinetic barrier than in the case of pure carbon growth (see Fig. 3 (b)).

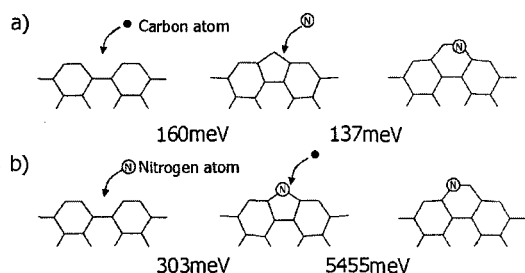


Fig. 4. Nitrogen incorporation into armchair growth front. Nitrogen goes into a) the second step and b) the first step of reaction.

Fig. 5 and Fig. 6 show all possible reaction paths when nitrogen is incorporated on the zigzag growth edge. On the zigzag edge, nitrogen can be incorporated in the stage of tetragon formation (Fig. 5 (a)), tetragon-pentagon transition (Fig. 5 (b)) or pentagon-hexagon transition (Fig. 6 (a)). If nitrogen is introduced in the first stage, reaction would occur along the path from Fig. 5. (a), (c), to (d). In this case, tetragon formation by nitrogen incorporation occurs without a kinetic barrier. Following reaction of carbon attachment to form a pentagon ring has a kinetic barrier of 154 meV, which is about 20 meV lower than in the case of pure carbon growth (see Fig. 3 (a)). Similar results were obtained when nitrogen is introduced at second step that follows a reaction path from Fig. 5. (b), (c), to (d). Tetragon formation with carbon has no kinetic barrier, and the nitrogen incorporation to the tetragon needs to overcome the kinetic barrier of 152 meV. Both paths have a common atomic configuration of pentagon ring shown in Fig. 5 (c).

Next reaction will generate two kinds of hexagon as shown in Fig. 5 (d), depending on the position of the added carbon atom. The added carbon can place at three distinguishable positions of pentagon ring, indicated by a, b and c in Fig. 5 (c). If the carbon atom is attached to

a or b site of pentagon, the upper configuration of Fig. 5

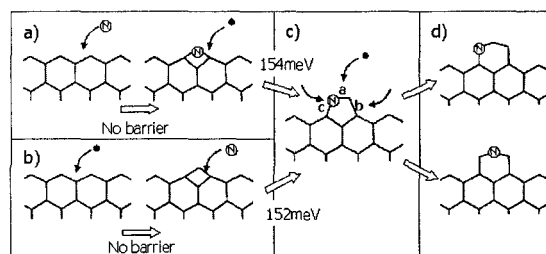


Fig. 5. Possible reaction paths for nitrogen incorporation on a zigzag edge. Nitrogen atom goes into the structure at the a) first step and b) second step of growth.

(d) would be obtained. The kinetic barrier for this reaction is 1 meV for a site and 0 meV for b site. If the carbon atom is attached on c site, the hexagon will have the configuration of the lower picture of Fig. 5. (d). However, this reaction needs to overcome the kinetic barrier of 743 meV, presumably due to the strong C-N bond. Hence, the upper configuration in Fig. 5 (d) would dominate the resulting hexagon structure that can be obtained without kinetic barrier.

Fig. 6 shows the reaction path when the nitrogen incorporation occurs in the stage of pentagon-hexagon transition. The growth sequence of pentagon ring formation is the same as that in pure carbon system shown in Fig. 3 (a). When the nitrogen is incorporated to the pentagon ring to form a hexagon ring, nitrogen atom can be placed at a or b site shown in Fig. 6. (a). Nitrogen incorporation at a site would result lower configuration in Fig. 6 (b), with the kinetic barrier of 88 meV. However, nitrogen incorporation at b site occurs without kinetic barrier resulting in the upper configuration of Fig. 6 (b). Even if the upper configuration is preferential, the advantage of nitrogen incorporation cannot be expected in this case.

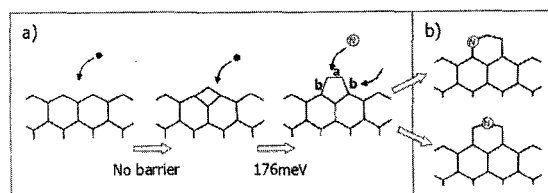


Fig. 6. Nitrogen incorporation during pentagon to hexagon transition on zigzag edge

As a result, nitrogen incorporation at first and second step is preferred in the case of zigzag edge. This value of the kinetic barrier is lower than that of the armchair edge (Fig. 4), which implies that the nitrogen incorporation would significantly occur in the zigzag edge. Furthermore, the kinetic barrier is reduced by about 20 meV from that in pure carbon growth.

3.2.2 Growth on Nitrogen Incorporated Growth Edge

Once the nitrogen atom is introduced into the carbon network, the nitrogen would affect the following reactions. After sequences of the growth reaction, the nitrogen can be placed on two distinguishable locations. One is the valley site, a concave shaped position between hexagon rings. The other is the top site, vertex

position of hexagon. Fig. 7 shows the possible configuration for armchair edge (Fig. 7 (a)) and zigzag edge (Fig. 7 (b)).

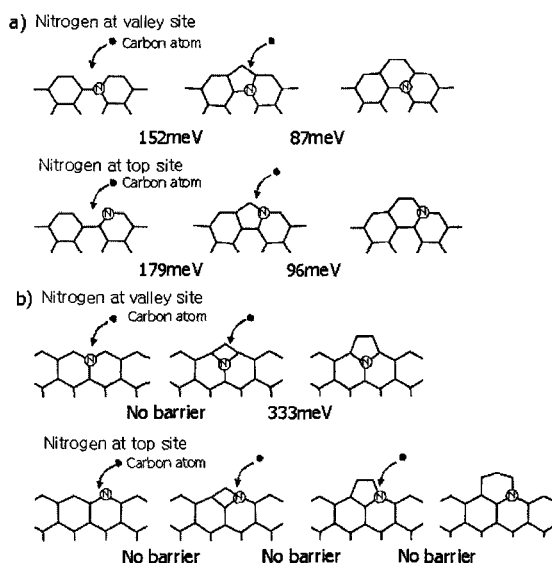


Fig. 7. The growth on nitrogen incorporated (a) armchair edge and (b) zigzag edge.

On the armchair edge, pentagon formation by one carbon atom attachment has the maximum kinetic barriers regardless of the position of the nitrogen. The maximum kinetic barriers are 152 meV when the nitrogen is placed at valley site (Fig. 7 (a)). If nitrogen locates at top site, the maximum kinetic barrier of the reaction is 179 meV. Fig. 7 (b) shows the schematic growth paths of zigzag edge with nitrogen. When the nitrogen is placed at valley site, tetragon-pentagon transition has very high kinetic barrier of 333 meV, whereas the tetragon formation occurs spontaneously once carbon atom is supplied. This seems to cause very stable tetragon, resulting in the defective structure of the CNT wall. When nitrogen locates on top site of zigzag edge, the kinetic barriers for all steps for additional hexagonal ring formation become zero.

It would be worth comparing the kinetic barriers with those of pure carbon nanotube growth. The nitrogen incorporation does not significantly affect the kinetic barrier of armchair edge growth. However, the kinetic barrier of zigzag edge growth disappears with the nitrogen in the carbon network. Consequently, the overall growth kinetics of the CNT would be governed by the armchair edge growth when nitrogen is incorporated. In contrast, the zigzag edge growth is the rate-limiting step for pure carbon nanotube growth.

Hence, the nitrogen incorporation would have an effect to reduce the kinetic barrier from 176 meV (see Fig. 3 (a)) to 152 meV (see upper configuration of Fig. 7 (a)). The previous experimental observations that the nitrogen incorporation enhanced the CNT growth would be a natural consequence of the reduced kinetic barrier by nitrogen.

4. CONCLUSIONS

Role of nitrogen incorporation in the CNT growth were investigated by first principles calculations. Total energy calculation of the strained tubular graphite sheet showed that the nitrogen incorporation does not play a role in relaxing the strain energy, if the diameter of CNT is larger than 35 Å. On the other hand, the nitrogen incorporation changed the rate-limiting growth step from zigzag edge growth for pure CNT to armchair edge growth. Because the kinetic barrier for armchair edge growth is much lower than that of zigzag edge growth, the CNT growth can be much enhanced by nitrogen incorporation.

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(Received December 9, 2003; Accepted April 20, 2004)