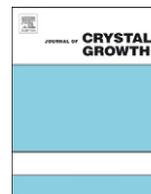




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Journal of Crystal Growth

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Base-growth mechanism of double-walled carbon nanotube in chemical vapor deposition



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ARTICLE INFO

Article history:

Received 30 June 2012

Received in revised form

22 December 2012

Accepted 3 February 2013

Communicated by J.M. Redwing

Available online 11 February 2013

Keywords:

A1. Growth models

A1. Nanostructures

A3. Chemical vapor deposition processes

B1. Nanomaterials

ABSTRACT

In this paper, a novel theoretical model based on phonon vibrations of the system is presented to explain base-growth of double-walled carbon nanotubes in chemical vapor deposition. In this regard, influence of interwall interaction and chirality on growth is also studied. Results of the presented theory are in good agreement with reported experimental results.

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1. Introduction

A new scientific field has been opened for researchers, after accidental discovery of carbon nanotubes (CNT) by Iijima [1] in 1991. Because of their structural [2], mechanical [3] and electronic unique properties, extensive research has been performed in identifying, synthesis and using CNTs in various industries [2–4]. These carbon nanotubes are used in high-strength composites [5], nanostructured electronic devices [6], nano-machines [7], etc. CNTs are divided into single-walled carbon nanotubes (SWCNTs), double-wall carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs). Because of DWCNT's unique structure [8], they have potential applications in electronic devices [9]. Most researches about DWCNTs, have studied the structural and electronic properties of DWCNTs, and have not presented an appropriate mechanism for growth of these structures. Several mechanisms for the growth of single-wall nanotubes are reported [10]. One of these mechanisms has been provided in our previous works [11,16,17] which presents an appropriate model for SWCNT growth based on phonon vibrations of tube on the substrate in chemical vapor deposition (CVD). In this paper, based on the phonon vibrations on catalyst and interlayer interaction, a

novel model for DWCNT growth in CVD is presented. Based on the theory, effect of diameter and temperature in DWCNT growth is investigated. Other parameters such as flow conditions, pressure and hydrocarbon type effect on growth [18–20] which are included in mean free path in our theory and diameter of CNT represents the effect of catalyst nanoparticle size on DWCNT growth. Simulations from the theory are in good agreement with reported experimental results.

Using the presented model one can obtain effective parameters in DWCNTs growth to optimize the growth conditions in future experimental works.

2. Interlayer interaction

In this paper, we consider double-wall carbon nanotubes as two coaxial cylinders, so that both of them vibrate on the substrate. In comparison with the carbon-carbon bonding energy in a graphene layer, interwall interaction energy of DWCNT is very small. Local density approximation [12], tight-binding method [13] and 6–12 Leonard–Jones potential [14] are some ways to expression the DWCNT interwall interaction. Here we use Leonard–Jones potential with $\varepsilon=2.968$ meV and $\sigma=3.407$ Å [14]

$$U_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

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where r is the distance between two against carbon atoms in two walls of DWCNT sample.

According to Eq. (1), we need to calculate the interwall distance to get the interwall interaction. We use the CNT radius equation, $R = a_0 \sqrt{3(n^2 + m^2 + nm)} / 2\pi$, to calculate the interwall distance, where $a_0 = 1.42 \text{ \AA}$ is the carbon–carbon bond length and (n, m) are the indices of the chiral vector [15]. When the relative displacement of the walls in the Z direction is zero, we consider this state as the initial state. So the distance between each pair of carbon–carbon in DWCNT for initial state, r_1 , is obtained by the following equation:

$$r_1 = R_{out} - R_{in} \quad (2)$$

By replacing r_1 in Eq. (1), one can obtain initial interwall interaction energy per carbon atom of DWCNT. When the distance between CNT and catalyst is more than the diameter of carbon atom, a carbon may sit between the catalyst and tube for a further growth of the tube [11]. It is thus expected the critical amplitude of CNT oscillation, A_{osc} , must be equal to the diameter of carbon atom for a further growth from the current stage. So when the relative displacement of the walls in the Z direction is equal to the diameter of carbon atom $D_c = 1.54 \text{ \AA}$, we consider this state as the final state. So the distance between each pair of carbon in DWCNT for final state, r_2 , is obtained by the following equation:

$$r_2 = \sqrt{r_1^2 + D_c^2} \quad (3)$$

By replacing r_2 in Eq. (1), one can obtain final interwall interaction energy per carbon atom of DWCNT. The initial interwall interaction energy is positive and the final interwall interaction energy is negative, so, by considering Eq. (4), the interwall interaction energy (U_{int}) is a negative energy which increases the oscillating energy of DWCNT's walls on substrate

$$U_{int} = U_{LJ}(r_2) - U_{LJ}(r_1) < 0 \quad (4)$$

Almost 25% of this energy (U_{int}) helps to increase the oscillating frequency of DWCNT's walls in Z direction and the remaining energy is spent for horizontal vibrations.

3. Growth model for inner and outer walls of DWCNT

Owing to the van der Waals bond with catalyst, the outer and inner walls of DWCNT oscillates longitudinally on catalyst during its growth. When the distance between a wall and catalyst is more than the diameter of carbon atom, a carbon may involve between the catalyst and tube for a further growth of the tube. It is thus expected the critical amplitude of CNT oscillation, A_{osc} , must be equal to the diameter of carbon atom for a further growth from the current stage. Van der Waals interaction between the inner and outer walls and also between the walls of DWCNT and its catalyst are simulated by the springs with different spring coefficients, meanwhile outer and inner CNTs are simulated by a mass $M_o(t)$ and $M_i(t)$, respectively, which are increasing during the growth in the theory. Fig. 1 is employed to illustrate the phonon vibrations of a DWCNT, its interaction with the catalyst and the interaction between walls by a spring–mass system [11,16].

The growth of a wall is described by loops and each loop is made of numbers of carbon atoms N . Therefore, the mass of the outer and inner walls and the numbers of carbon atoms in one loop in each wall are written as,

$$M_o(t) = n_o(t)N_o m_c \text{ and } M_i(t) = n_i(t)N_i m_c \text{ where}$$

$$N_o = \frac{\pi D_o}{d_{C-C}} \text{ and } N_i = \frac{\pi D_i}{d_{C-C}} \quad (5)$$

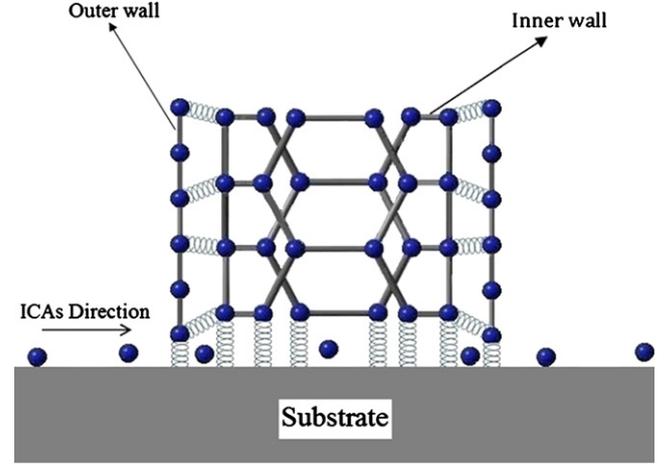


Fig. 1. Simulation of DWCNT growth. Interwall interaction and interaction between DWCNT and substrate are simulated by spring. Carbon atom is simulated by blue spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where $n(t)$, m_c , D and d_{C-C} are the number of loops that is increasing during the growth, the mass of a carbon atom, the CNT diameter and carbon–carbon bond length in each loop, respectively. Because only the first loop interacts with catalyst, the spring coefficient representing the van der Waals interaction between each wall and substrate, K , is provided to be

$$K_o = N_o k_o, K_i = N_i k_i \quad (6)$$

where $k = 2E_{osc} / A_{osc}^2$, and E_{osc} and k are the energy of oscillation and spring coefficient between a carbon atom and the catalyst, respectively. Oscillation energy for each wall of DWCNT is a combination of energy between the wall and the catalyst, E_{sub} , and interwall interaction energy, E_{int} , as

$$E_{osc} = E_{sub} + E_{int} \quad (7)$$

The relation of E_{osc} with temperature, T , and van der Waals bond energy between CNT and catalyst, U_{LJ} , is provided to be,

$$E_{osc} = E_0 \exp\left(\frac{U_{LJ}}{k_B T}\right), \quad (8)$$

where U_{LJ} is Lennard–Jones potential. If E_0 , in comparison with U_{LJ} , is large, CNT cannot oscillate and will be detached from catalyst. Therefore, $E_0 = 0.01 |U_{LJ}|$ is proposed in the model.

To obtain the interwall interaction energy, we should first obtain the number of carbon–carbon van der Waals bonds between outer and inner walls. Certainly, the number of bonds will not be more than number of carbon atoms on the inner wall. Also, all the carbon atoms on the inner wall, will not link to outer wall atoms at the same time. Therefore we use geometric mean to approximate the van der Waals bonds [21]

$$\text{Number average of van der Waals bonds} = \sqrt{(\alpha N_i) n_i} \quad (9)$$

where n_i and N_i are number of loops and number of carbon atoms in each loop of inner wall and $\alpha = 6 \times 10^{-15}$ is the number of link per carbon atom in two graphene layer [18].

E_{int} , average interaction energy between two walls is obtained by the following equation:

$$E_{int} = \sqrt{\alpha N_i n_i} (0.25 U_{int}) \quad (10)$$

It is obvious that the number of loops, $n(t)$, is a function of the angular frequency of the oscillation, $\omega(t)$, and time, which is shown in the following expression:

$$n(t) = \frac{\omega(t)}{2\pi N} t \quad (11)$$

where $\omega(t) = \sqrt{2E_{osc}/n(t)A_{osc}^2 m_c}$. $n(t)$ can be calculated from Eq. (11), and the length of the each DWCNT wall is provided to be,

$$L_o(t) = n_o(t)l_c, \quad L_i(t) = n_i(t)l_c \quad (12)$$

where $L(t)$, l_c are CNT length and distance between two loops, respectively. Eq. (12) is obtained without considering the damping effect. To consider the effect of damping due to the environment and any other loss in the system, Eq. (12) should be multiplied by $e^{-\gamma t}$ that demonstrates the effect of damping on growth process. The parameter γ is damping factor which depends directly on pressure. In this study, it is assumed that system pressure is constant.

The postulation employed in the theory is that the velocity of the immigrant carbon atoms (ICAs), V , is not infinity. ICA is a free carbon which is realized from a hydrocarbon molecule by thermal decomposition. If l_{mfp} is the mean free path between the two ICAs, shown in Fig. 1, and ICAs have three degrees of freedom, we can write the following equation,

$$\frac{3}{2}k_B T = \frac{1}{2}m_c V^2, \quad (13)$$

where β is a coefficient, representing the probability of binding an immigrant carbon atom to CNT in a period of CNT oscillation, which is considered in the theory. For outer wall, β is as follows:

$$\beta_o = \frac{t_c}{(T_{osc})_o}, \quad (14)$$

where $t_c = l_{mfp} \sqrt{m_c/3k_B T}$ and T_{osc} is period of oscillation.

By replacing Eqs. (4)–(14) in Eq. (12), the time-dependent equation of outer wall length is obtained as:

$$L_o(t) = l_c \sqrt{\frac{t_c(0.01N_o|U_{LJ}|e^{2U_{LJ}/k_B} + \sqrt{\alpha N_i n_i(0.25U_{int})})}{2\pi^2 m_c N_o^2 A_{osc}^2}} t^{1/2} e^{-\gamma t} \quad (15)$$

According to Eq. (15), the outer wall length depends on the number of inner wall loops.

In following, we will study time-dependent of inner wall growth mechanism. All stages of calculations for inner wall are similar to the calculations for outer wall, except that the probability of binding an ICA to inner wall defined by β_i .

$$\beta_i = q \left(1 - \frac{t_c}{(T_{osc})_o}\right) \frac{t_c}{(T_{osc})_i} \quad (16)$$

where $q(1 - t_c/(T_{osc})_o)$ is the probability of transmission of ICA from the outer wall. q is the coefficient of decreasing effect of outer layer on inner layer growth.

Therefore, this change can be applied to achieve the number of loops of inner wall as

$$n_i^4 - 2atn_i^2 - b^2 t^2 n_i + a^2 t^2 = 0 \quad (17)$$

where

$$a = qt_c \left(1 - \frac{t_c}{(T_{osc})_o}\right) \left[\frac{0.01|U_{LJ}|e^{2U_{LJ}/k_B}}{2\pi^2 m_c N_i A_{osc}^2} \right]$$

$$b = qt_c \left(1 - \frac{t_c}{(T_{osc})_o}\right) \left[\frac{\sqrt{\alpha N_i(0.25|U_{int}|)}}{2\pi^2 m_c N_i A_{osc}^2} \right]$$

Eq. (17) has four answers which one of them is acceptable. By replacing the acceptable answer in Eq. (12), time-dependent of inner wall growth equation will be obtained.

Results of the theory for both inner and outer walls and experimental diagram of DWCNT growth are shown in Fig. 2. Theoretical diagrams are plotted for (5,5)/(10,10) DWCNT sample by using Eqs. (12) and (14) with following parameters: $T=998$ K, $A_{osc}=1.54$ Å, $l_{mfp}=4$ Å, $k_B=1.381 \times 10^{-23}$ J/K, $m_c=19.926 \times 10^{-27}$ kg, U_{LJ} (between carbon and iron)=2.402 kJ/mol, $l_c=1.5$ Å, $d_{C-C}=1.44$ Å and $\gamma=1.2 \times 10^{-4}$ s $^{-1}$.

Fig. 2(a) shows the growth of DWCNT walls will be saturated which is in agreement with reported experimental results in Fig. 2(b) [22]. It is due to increase of inertia and also increase of system damping during the length increasing. However, there is a

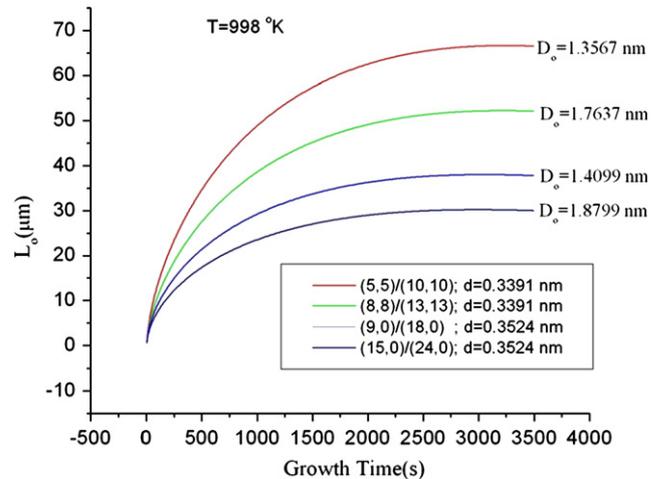


Fig. 3. Variations of outer wall length of DWCNT as a function of reaction time for different diameters.

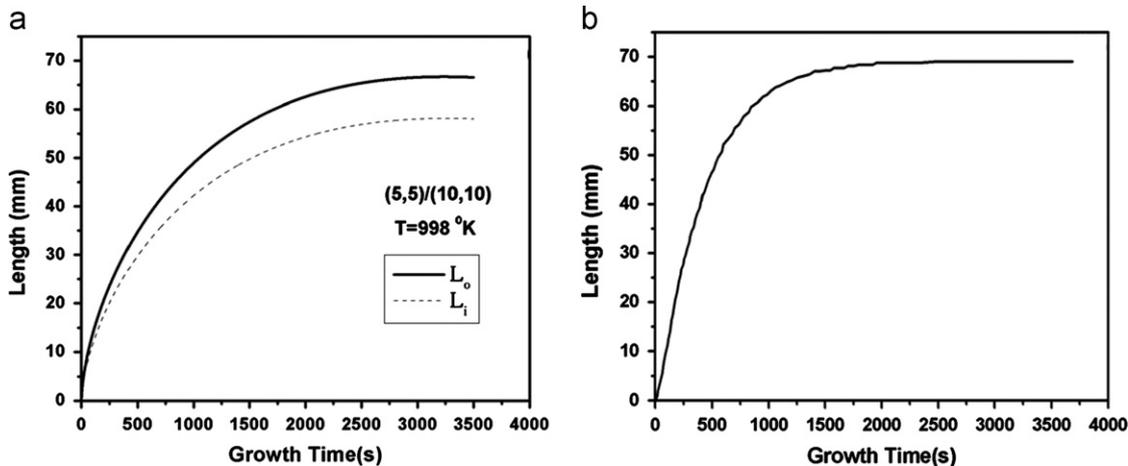


Fig. 2. (a) Obtained results of the theory for variation of outer (L_o) and inner (L_i) wall length as a function of reaction time at $T=998$ K, (b) Reported experimental results for outer wall growth of DWCNT with $T=998$ K, feed stock gas C_2H_2 , catalyst nanoparticle (Fe/Mo), flow rate 2 sccm [22].

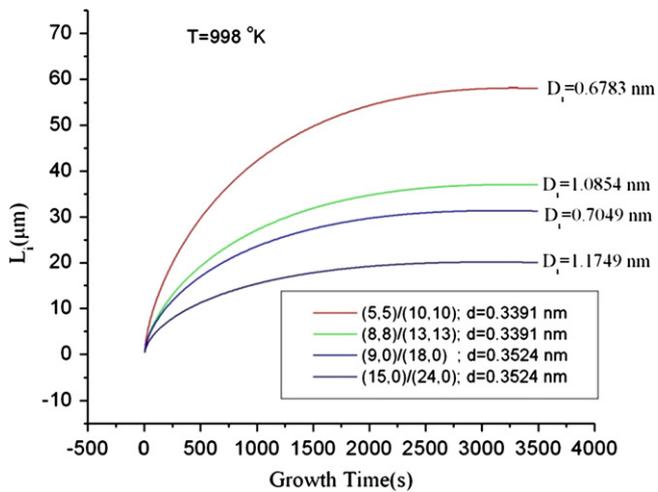


Fig. 4. Variations of inner wall length of DWCNT as a function of time for different diameters.

little difference between the theoretical and experimental results in first 500 s of growth which is because of assuming the damping factor as a constant in the theory but in reality, it varies with the increasing of the length.

It is important to note that, in the presented theory, flow rate, pressure and hydrocarbon type effect on mean free path which is considered as a constant in our calculations. Also diameter of CNT represents the effect of catalyst nanoparticle size on DWCNT growth.

3.1. DWCNT growth with different diameters

Variations of outer and inner wall length as a function of reaction time for different diameters are plotted in Figs. 3 and 4. Parameter d is the distance between outer and inner walls. As the figures show, DWCNTs with larger diameter are saturated more rapidly. The observations are discussed and interpreted as follows. First, because a CNT with larger diameter has more effective surface area, it is more affected by damping factors than CNTs with smaller diameter. Second, a CNT with larger diameter has higher inertia and consequently leads to lower frequency of CNT vibration. In addition, Figs. 3 and 4 show another important result; armchair samples grow more than zigzag samples. This phenomenon occurs because in addition to diameter, the distance between walls is a main factor. As it is shown in Figs. 3 and 4, the

distance between walls in zigzag samples is larger than armchair samples and so, according to Eqs. (2)–(4), interaction energy between inner and outer walls of zigzag DWCNT is weak and its growth is saturated more rapidly.

4. Conclusions

In this paper, a theoretical model based on phonon vibrations of the system was presented to explain base-growth of double-walled carbon nanotubes in chemical vapor deposition. Influence of interwall interaction and chirality on growth was studied and compared to reported experimental results. It was shown that DWCNTs with larger diameter grow less. In addition, results demonstrated that zigzag DWCNTs grow less than armchair DWCNTs in the same situation. Results of the theory were discussed and physical reasons for observations were presented.

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