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Theoretical investigation of the growth rate of carbon nanotubes in chemical vapor deposition

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Abstract

The growth rate of carbon nanotubes in chemical vapor deposition is simulated by using a theoretical analysis of the phonon vibration of the system. Simulations demonstrate that the growth rate of carbon nanotubes with larger diameters is smaller because of higher damping factors and carbon nanotube inertia. An optimum temperature for the growth rate is calculated for a carbon nanotube on Fe catalyst. Simulations from the theory are in good agreement with reported experimental results.

Keywords: Carbon nanotube; chemical vapor deposition; growth rate; optimum temperature

1. Introduction

Carbon nanotubes (CNTs) are a recently discovered form of carbon with a graphitic lattice and a long, tubular structure [1]. Their remarkable electrical, mechanical, and thermal properties [2, 3] enable them to be used for the development of devices for nanoelectromechanical and nanophotovoltaic system applications. In order to fully optimize the production of CNTs, the growth mechanisms involved in their formation must be completely understood, and a number of theories have been proposed to describe their growth [4-11]. Bower *et al*. [12] presented a mechanistic study of the nucleation and growth of aligned nanotubes by microwave plasma chemical vapor deposition (CVD). They found that nanotubes grow initially at a very rapid rate, followed by a dramatic decrease in growth. In view of the experimental and simulation works, a comprehensive study to describe the growth mechanism and reveal the effect of parameter variables, such as the temperature, on the CNT growth rate is indispensable. This paper reports a theoretical model for the growth of a CNT on catalyst to provide an investigation on the growth rate of CNTs in CVD. The effect of temperature on growth rate is particularly investigated.

2. Theoretical investigation

Owing to the van der Waals bond with catalyst, a CNT oscillates longitudinally on a catalyst during its growth. When the van der Waals force minimizes, a carbon may involve between the catalyst and tube for a further growth of the tube [8, 9]. It is thus expected that the critical amplitude of CNT oscillation, $A_{osc,}$ must be equal to the diameter of the carbon atom for a further growth from the current stage. Van der Waals interaction between CNT and its catalyst is simulated by a spring, meanwhile a CNT is simulated by a mass *M(t)* which is increases during the growth in the theory. Figure (1) is employed to illustrate the phonon vibration of a CNT and its interaction with the catalyst by a spring- mass system.

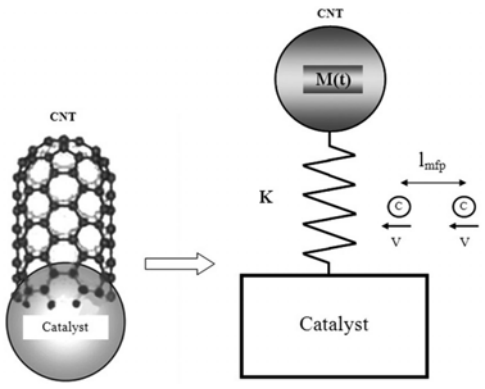

Fig. 1. Model of CNT and its catalyst by a mass-spring system

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

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$$M(t) = n(t)Nm_C \quad \text{and} \quad N = \frac{\pi D}{d_{C-C}}, \tag{1}$$

where $n(t)$, m_C, D and $d_{C\text{-}C}$ are the number of loops that is increase during the growth, the mass of a carbon atom, the CNT diameter and carbon-carbon bond length, respectively. Because only the first loop interacts with catalyst, the spring coefficient representing the van der Waals effect, K, is provided as,

$$K = Nk, \tag{2}$$

where $k = \frac{2E_{osc}}{A_{osc}^2}$, and E_{osc} and k are the energy of oscillation and spring coefficient between a carbon atom and the catalyst, respectively. 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:

$$n(t) = \frac{\omega(t)}{2\pi N}t. \tag{3}$$

where $\omega(t) = \sqrt{\frac{2E_{osc}}{n(t)A_{osc}^2 m_C}}$. From Eq. (3), $n(t)$ can be calculated, and the growth of the CNT is provided as,

$$L(t) = n(t)l_c, \tag{4}$$

where $L(t)$, l_C are CNT length and distance between the two loops, respectively. Eq. (4) 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. (4) should be multiplied by $e^{-\gamma t}$, which demonstrates the effect of damping on growth. The postulation employed in the theory is that the velocity of the immigrant carbon atoms, V, is not infinity. If l_{mfp} is the mean free path between the two immigrant carbon atoms, shown in Fig. 1, and immigrant particles have three degrees of freedom, we can have the following equation,

$$\frac{3}{2}k_B T = \frac{1}{2}m_c V^2, \tag{5}$$

A coefficient β, representing the probability of binding an immigrant carbon atom to CNT in a period of CNT oscillation, is considered in the theory as follows:

$$\beta = \frac{t_c}{T_{osc}}, \tag{6}$$

where $t_c = l_{mfp}\sqrt{\frac{m_C}{3k_B T}}$ and T_{osc} is the period of oscillation. Also, the relation of E_{osc} with temperature T and van der Waals bond energy between the CNT and catalyst U_{LJ} is provided as,

$$E_{osc} = E_0 \exp(\frac{U_{LJ}}{k_B T}), \tag{7}$$

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 the catalyst. Therefore, $E_0 = 0.01|U_{LJ}|$ is proposed in the model. The expression for growth rate is finally obtained from Eqs. (3)-(7) as follows,

$$\frac{dL}{dt} = \sqrt{\frac{l_{mfp}|U_{LJ}|e^{\frac{2U_{LJ}}{k_B T}}d_{C-C}}{(3)^{\frac{1}{2}}200\pi^3 DA_{osc}^2 m_C^{\frac{1}{2}}}}(k_B T)^{\frac{-1}{4}}l_C(\frac{1}{2\sqrt{t}} - \gamma\sqrt{t})e^{-\gamma t}. \tag{8}$$

3. Results

3.1 Growth rate of CNT with different diameters

The variation of the growth rate of the CNT with different diameters versus time, based on Eq. (8), is plotted in Fig. (2) with the following parameters: A_{osc}=0.77 Å, l_C=1.5 Å, $d_{C\text{-}C}$=1.44 Å, m_C=19.926×10^{-27} Kg, l_{mfp}=4 Å, γ=1.2×10^{-4} s^{-1}, $|U_{LJ}|$ (between carbon and iron) =2.402 Kj/mol and T=700 ^{o}C [13].

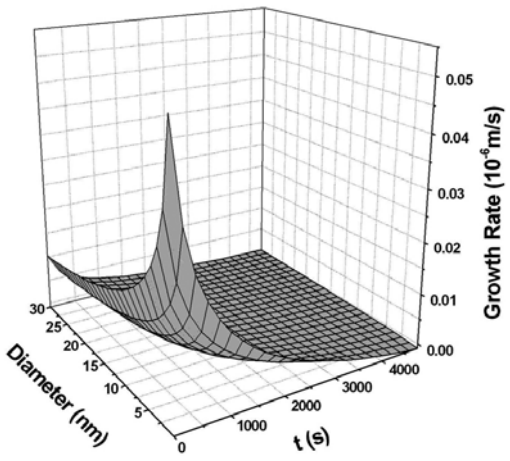

Fig. 2. Growth rate of CNTs as a function of reaction time and diameter of CNTs

According to Fig. (2), the growth rate of the CNTs decreases, which was also demonstrated experimentally by Lee *et al.* [14]. In addition, it is found that the growth rate of CNTs with larger diameters decreases more rapidly. The observations

are discussed and interpreted as follows. First, because a CNT with a larger diameter has a more effective surface area, it is more affected by damping factors than CNTs with smaller diameters. Second, a CNT with a larger diameter has higher inertia, and consequently leads to a lower frequency of CNT vibration.

3.2 Dependence of temperature on CNT growth rate

Next, Fig. (3) is provided to describe the variation of the growth rate of CNT with different diameters versus the temperature with the parameters A_{osc}=0.77 Å, l_C=1.5 Å, $d_{C\text{-}C}$=1.44 Å, m_C=19.926×10^{-27} Kg, l_{mfp}=4 Å, γ=1.2×10^{-4} s^{-1}, $|U_{LJ}|$ (between carbon and iron) =2.402 Kj/mol and t=20 min.

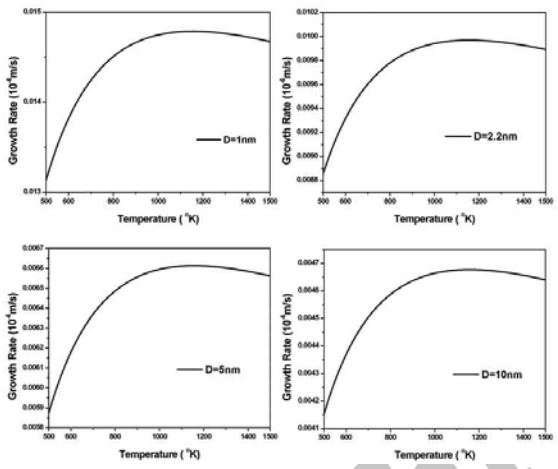

Fig. 3. Dependence of temperature on growth rate of CNTs with different diameters

Figure (3) indicates that there is a temperature which optimizes the growth rate of CNT. For example, for the growth rate of a CNT on iron, the optimum temperature is about 973 K. Similar observations were also verified by experimental works [13, 15-20]. From Eqs. (5)-(7), when temperature goes up, the oscillation energy of CNT increases. Such an increase in oscillation energy is faster than the increase of velocity of immigrant particles, and hence the growth is fastened accordingly. However, after a specific temperature, the energy increase will be slower than the increase of carbon atom velocity and consequently β will decrease, leading to slower growth. The optimum temperature can be calculated for obtaining the maximum length of the CNTs.

4. Conclusions

The paper reports a theory for the growth of a CNT on catalyst. The CNT growth rate decreases due to damping factors and CNT inertia. It is demonstrated that at a specific temperature, the growth rate of CNTs with larger diameters decreases more rapidly because of higher CNT inertia. Finally, the relationship between the CNT growth rate and the temperature of growth demonstrates the existence of an optimum temperature for optimizing the growth rate of CNTs.

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بررسی نظری نرخ رشد نانولوله های کربنی در رسوب بخار شیمیایی

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چکیده:

نرخ رشد نانو لوله های کربنی در رسوب بخار شیمیایی، با استفاده از یک آنالیز نظری روی نوسانات فونونی سیستم، شبیه سازی می شود. شبیه سازی ها نشان می دهد که نرخ رشد نانو لوله های کربنی با قطر بزرگتر، بواسطه داشتن شاخص میرایی و لختی بالاتر، کمتر است. برای نرخ رشد یک نانولوله کربنی روی کاتالیست آهن، یک دمای بهینه محاسبه می شود. نتایج شبیه سازی های بدست آمده از نظریه مورد نظر در توافق خوبی با نتایج تجربی گزارش شده می باشد.

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