

# Low-temperature growth mechanism of Silicon 1-D structure

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A novel model is presented to explain the low-temperature growth mechanism of silicon nanotube (SiNT) in catalytic chemical vapor deposition. The developed model is based on kinetic theory of gases and phonon vibrations of SiNT on catalyst and is in agreement with reported experimental works. Simulations demonstrate that the SiNT can grow more than  $5\mu\text{m}$  and growth is saturated at a certain time. Also investigations show the existence of an optimum temperature and an optimum catalyst for growth process. Finally, effect of the partial pressure of decomposed feedstock gas on the SiNT growth is presented.

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## 1. Introduction

Since the existence of carbon nanotubes (CNTs) has been reported by Iijima [1] and their wide applications in sciences and technologies [2-6] investigation of properties, fabrication methods and application of nanotubes produced from other materials has been begun because of their unique physical and chemical properties [7-13]. One of these useful nanostructures is silicon nanotube (SiNT) produced from silicon which widely recognized as the most important material of the recent centuries. According to the relation between SiNT structure and its physical and chemical properties [14, 15], control and optimization of synthesis methods of this structure and study of effective parameters in its growth are the most important subjects in SiNT science. To approach this aim, their growth mechanism in various production methods must be understood. Compared to other production methods, chemical vapor deposition (CVD) is the most practical production method [16, 17]. Up to now, some studies have been done to investigate some concepts of growth mechanism of CNTs i.e. preparation mechanism of catalyst and substrate to start growing [18-22], conditions for base-growth and tip-growth [23, 24], growth mechanism of SWCNT and DWCNT [25-30], influence of external fields on CNT growth [31-33], etc. But there is not any proper and scientific model to describe the growth mechanism of SiNT.

In this paper, based on the phonon vibrations of SiNT on catalyst and kinetic theory of gases, a novel model is offered to describe the low-temperature growth of a single SiNT in catalytic CVD. Based on the theory, effect of SiNT diameter, growth temperature, type of catalyst and partial pressure of decomposed feedstock gas on growth is investigated. In the model, diameter of SiNT represents the effect of catalyst nanoparticle size on SiNT growth. Predictions of the model are useful for optimizing the growth conditions in future experimental works.

## 2. Physical model

The structure of presented model is similar to the model presented for base-growth of SWCNT in CVD [25] with fundamental changes and scientific corrections according to the silicon atoms and production method. A SiNT oscillates on catalyst during its growth because of the physical bond with catalyst. In base growth regime, a silicon atom of decomposed feedstock gas can bond to the growing tube when the distance between SiNT and catalyst is more than the diameter of silicon atom. Thus, it is reasonable for assuming that the critical amplitude of SiNT oscillation,  $A_{osc}$ , must be equal to the diameter of silicon atom. Physical interaction between the SiNT and its catalyst is investigated by Lennard-Jones potential which is simulated by a spring, meanwhile a SiNT is simulated by a mass  $M(t)$  which is increasing during the growth in the model. Fig. 1 illustrates the system of catalytic CVD and employed simulation for the phonon vibrations of a SiNT on catalyst schematically.

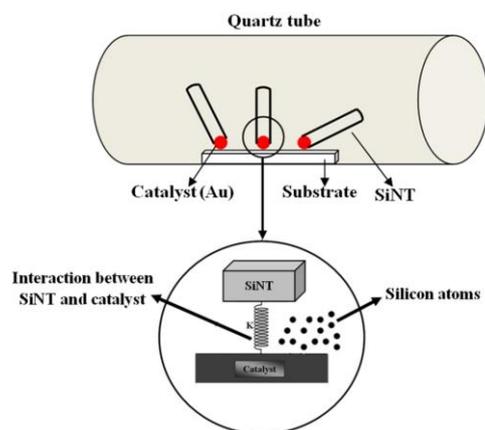


Fig. 1. Schematic of SiNT growth in catalytic CVD and employed simulation

In the model, it is assumed that a SiNT is formed by some loops,  $n(t)$ , increasing during the growth and each loop is made of numbers of silicon atoms  $N$ . So,  $M(t)$  and  $N$  can be written as,

$$M(t) = n(t)Nm_{Si}; N = \frac{\pi D}{d_{Si-Si}} \quad (1)$$

where  $m_{Si}$ ,  $D$  and  $d_{Si-Si}$  are the mass of a silicon atom, the SiNT diameter and silicon-silicon bond length in each loop, respectively. The spring coefficient simulating the physical bond between a silicon atom and the catalyst,  $k$ , is considered to be

$$k = \frac{2E_{osc}}{A_{osc}^2} \quad (2)$$

where  $E_{osc}$  is energy of oscillation of SiNT. In the model, the number of loops depends on growth time,  $t$ , and period time of nanotube vibration,  $T_{osc}$ , as following equation:

$$n(t) = \frac{t}{T_{osc}N} \quad (3)$$

where  $T_{osc} = \sqrt{\frac{2\pi^2 n(t) A_{osc}^2 m_{Si}}{E_{osc}}}$ . So the growth of the SiNT is presented by

$$L(t) = n(t)l_{Si}e^{-\eta t} \quad (4)$$

where  $L(t)$  and  $l_{Si}$  are SiNT length and distance between two loops, respectively. The term  $e^{-\eta t}$  relates to damping effects in the system and  $\eta$  is damping factor.

The syllogism used in the model is that the thermal velocity of the decomposed silicon atoms produced by feedstock decomposition,  $V_T$ , is not infinity. From kinetic theory, if decomposed atoms have three degrees of freedom, the thermal velocity will relate to growth temperature as below

$$\frac{3}{2}k_B T = \frac{1}{2}m_{Si}V_T^2 \quad (5)$$

Also the probability of binding a decomposed silicon atom to each wall is represented by  $\beta$ :

$$\beta = \frac{t_{c(\min)}}{t_c} \quad (6)$$

where  $t_c$  is time interval between two decomposed silicon atoms and can be obtained by

$$t_c = \frac{l_{mfp}}{V_T} \quad (7)$$

where  $l_{mfp} = \frac{1}{\sqrt{2}\pi d^2 n_v}$  is mean free path between the two decomposed silicon atoms.  $d$  which is equal to the

amplitude of oscillation is diameter of silicon atom. In the model, the gas of decomposed silicon atoms is considered as an ideal gas because of low partial pressure in quartz tube. So, the  $n_v$  is equal to  $P/(k_B T)$ . The parameter  $P$  is partial pressure of decomposed feedstock gas. The constant parameter  $t_{c(\min)}$  in Eq.(6), is minimum significant time interval between the two decomposed silicon atoms which is considered equal to  $10^{-12}$ s. Also the relation of  $E_{osc}$  with growth temperature,  $T$  and physical bond energy between SiNT and catalyst,  $U_{LJ}$ , is considered as,

$$E_{osc} = E_0 \exp\left(\frac{\gamma U_{LJ}}{\frac{1}{2}k_B T}\right) \quad (8)$$

where  $U_{LJ}$  and  $\gamma$  are Lennard-Jones potential and heat capacity ratio, respectively. If  $E_0$ , in comparison with  $U_{LJ}$ , is large, SiNT cannot oscillate and will be disconnected from catalyst. So,  $E_0 = 0.01|U_{LJ}|$  is supposed in the model. Finally, the equation of growth is achieved from Eqs. (1) – (8) as below,

$$L = \left(\frac{0.03A_{osc}d_{Si-Si}t_{c(\min)}\sqrt{U_{LJ}}e^{\frac{\gamma U_{LJ}}{k_B T}}}{\pi D m_{Si}}\right)^{\frac{2}{3}} \left(\frac{P}{k_B T}\right)^{\frac{1}{3}} t^{\frac{2}{3}} e^{-\eta t} l_{Si} \quad (9)$$

### 3. Results

#### 3.1. SiNT growth with various diameters

The length of the SiNT with various diameters as a function of time is illustrated in Fig. 2 by using Eq. (9) and following parameters:  $A_{osc}=1.11 \text{ \AA}$ ,  $l_{Si}=2.2 \text{ \AA}$ ,  $d_{Si-Si}=2.2 \text{ \AA}$ ,  $k_B=1.381 \times 10^{-23} \text{ J/K}$ ,  $t_{c(\min)}=10^{-12} \text{ s}$ ,  $m_{Si}=46.636 \times 10^{-27} \text{ Kg}$ ,  $\eta=8 \times 10^{-4} \text{ s}^{-1}$ ,  $U_{LJ}$  (between silicon and gold) = -1.358KJ/mol,  $\gamma$  (for ideal gas) =  $\frac{5}{3}$ ,  $P=0.152 \text{ Torr}$  and  $T=420^\circ \text{C}$ .

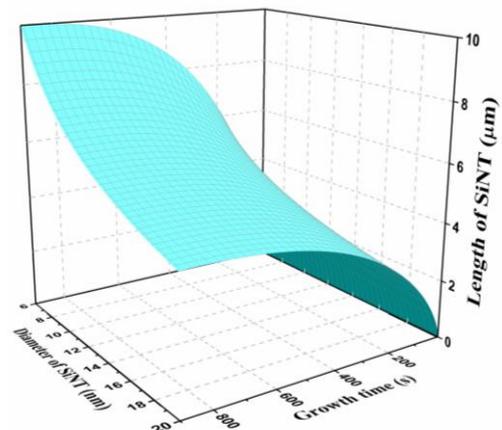


Fig. 2. Growth of SiNTs with various diameters at  $P=0.152 \text{ Torr}$  and  $T=420^\circ \text{C}$

Fig. 2 shows that there is not any observable growth in the first seconds. But after 13 min, SiNT length can reach more than  $5\mu\text{m}$  and the growth of SiNTs is saturated after a specific moment, which were also demonstrated experimentally [16, 17].

### 3.2. Optimum catalyst and temperature for growth of SiNT

Fig. 3 is plotted to show the variation of the maximum length of grown SiNT as a function of the growth temperature and Lennard-Jones potential by using the Eq. (9) and the following parameters  $A_{osc}=1.11 \text{ \AA}$ ,  $l_{Si}=2.2 \text{ \AA}$ ,  $d_{Si-Si}=2.2 \text{ \AA}$ ,  $k_B=1.381\times 10^{-23} \text{ J/K}$ ,  $t_{c(\text{min})}=10^{-12} \text{ s}$ ,  $m_{Si}=46.636\times 10^{-27} \text{ Kg}$ ,  $\eta=8\times 10^{-4} \text{ s}^{-1}$ ,  $\gamma \text{ (for ideal gas)}=\frac{5}{3}$ ,  $P=0.152 \text{ Torr}$ ,  $D=14 \text{ nm}$  and  $t=15 \text{ min}$ .

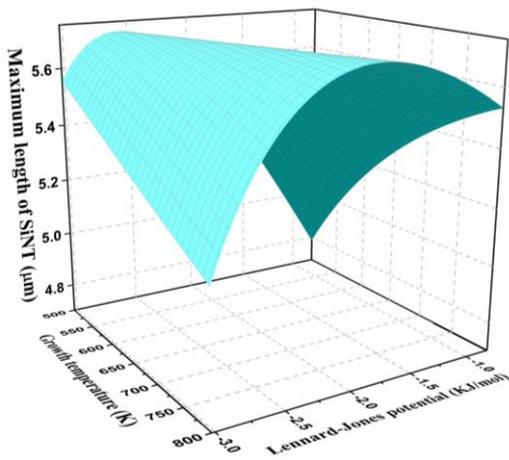


Fig. 3. Dependence of temperature and catalyst type on growth of SiNT

Fig. 3 shows that there is a certain temperature which optimizes the growth of SiNT. For example, for the growth of SiNT with gold as catalyst, the optimum temperature is about  $420 \text{ }^\circ\text{C}$ . Similar observations were also confirmed experimentally [16, 17]. Also Fig. 3 illustrates that there is an optimum catalyst for SiNT growth at each temperature. Existence of an optimum catalyst to optimize SiNT growth has also been reported in some papers [16, 17].

### 3.3. Influence of partial pressure on SiNT growth

Fig. 4 shows the variation of maximum length of SiNT versus diameter of SiNT and partial pressure by using the Eq. (9) and the following parameters  $A_{osc}=1.11 \text{ \AA}$ ,  $l_{Si}=2.2 \text{ \AA}$ ,  $d_{Si-Si}=2.2 \text{ \AA}$ ,  $k_B=1.381\times 10^{-23} \text{ J/K}$ ,  $t_{c(\text{min})}=10^{-12} \text{ s}$ ,  $m_{Si}=46.636\times 10^{-27} \text{ Kg}$ ,  $\eta=8\times 10^{-4} \text{ s}^{-1}$ ,  $U_{LJ}$  (between silicon

and gold) =  $-1.358 \text{ KJ/mol}$ ,  $\gamma \text{ (for ideal gas)}=\frac{5}{3}$ ,  $T=420^\circ\text{C}$  and  $t=15 \text{ min}$ .

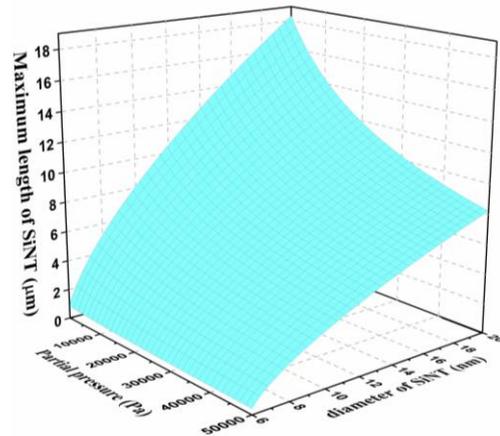


Fig. 4. Dependence of partial pressure on SiNT growth

As it is shown in the Fig. 4, when the partial pressure of decomposed feedstock gas goes up, the length of SiNT increases. Similar observations are also reported by experimental works [16]. As Fig. 4 shows, for SiNT with smaller diameter, influence of partial pressure on SiNT length is more.

## 4. Discussion

In Fig. 2, the growth of SiNT is saturated because of increasing of mass during the growth and consequently, decreasing the frequency of SiNT oscillation. In addition, damping factors such as friction are other reasons of growth saturation. Also it is shown that SiNTs with larger diameter are saturated more rapidly. The observations are discussed and interpreted as follows. First, because a SiNT with larger diameter has more effective surface area, it is more affected by damping factors. Second, a SiNT with larger diameter has higher inertia which leads to the SiNT vibration with lower frequency.

Also, the results illustrated in the Fig. 3 can be explained scientifically. Increasing of temperature leads to increase of the oscillation energy. So the growth is accelerated accordingly. However, after the optimum temperature, increase of the energy is slower than the increase of time interval between two decomposed silicon atoms,  $t_c$ , and therefore, binding probability,  $\beta$ , will be reduced which causes slower growth. The optimum temperature can be calculated for obtaining the maximum length of SiNTs. The model predicts that if a catalyst with stronger interaction with SiNT is employed, the optimum growth temperature can be adjust even to lower than  $250 \text{ }^\circ\text{C}$  and consequently, leads to energy conservation. Also as Fig. 3 demonstrates, there is an optimum catalyst for SiNT growth at each temperature. Regarding to the presented model, the  $E_{osc}$  is increased by the increase of the physical

bond energy up to a certain value. After this value, the oscillation energy is reduced because, at this situation, the bond energy between the silicon and its catalyst is higher than thermal energy which is received by the SiNT. So, the SiNT motion is restricted and, therefore, the growth process is perturbed.

According to the Eq. (9), increasing partial pressure leads to reducing mean free pass of silicon atoms and therefore,  $t_c$  is reduced. Consequently,  $\beta$  increases and, as Fig. 4 demonstrates, SiNT grows more. Although increasing partial pressure leads to increasing  $\beta$ , but, for SiNT with larger diameter, more silicon atoms must be bonded to complete a loop in SiNT. So, as Fig. 4 shows, for SiNT with smaller diameter, influence of partial pressure on SiNT length is more.

## 5. Conclusion

In this paper a novel model based on kinetic theory of gases and phonon vibrations of SiNT on catalyst was presented to explain base-growth of SiNT in catalytic CVD. Results show that although the SiNT can grow more than 5  $\mu\text{m}$ , but also the growth of SiNT is saturated after a specific moment. Furthermore, influence of temperature and type of catalyst on growth was discussed and it was shown that there is an optimum temperature and an optimum catalyst for growth process. Finally, investigation of effect of the partial pressure of decomposed feedstock gas on SiNT growth shows that increasing of partial pressure leads to longest SiNTs and influence of partial pressure on SiNTs with smaller diameter is stronger. Because all results of the presented mechanism are in good agreement with reported experimental results, so predicted concepts of SiNT growth can be useful in future experimental and theoretical researches for optimization of SiNT growth.

The author does not have any conflict of interests.

## References

- [1] S. Iijima, *Nature* **354**, 56(1991).
- [2] E. Mohammadi-Manesh, M. Vaezzadeh, M. Saeidi, *Computat Mater Sci* **97**, 181 (2015).
- [3] E. Mohammadi-Manesh, M. Vaezzadeh, M. Saeidi, *Surf. Sci.* **636**, 36 (2015).
- [4] M. Vaezzadeh, M. R. Saeedi, T. Barghi, M. R. Sadeghi, *Chem. Cent. J* **1**, 22 (2007).
- [5] W. A. de Heer, A. Chatelain, D. A. Ugarte, *Science* **270**, 1179 (1995).
- [6] A. Bachtold, P. Hadley, T. Nakanishi, C. Dekker, *Science* **294**, 1317 (2001).
- [7] R. T. Senger, S. Dag, S. Ciraci, *Phys. Rev. Lett.* **93**, 196807 (2004).
- [8] Y. Li, J. Wang, Z. Deng, Y. Wu, X. Sun, D. Yu, P. Yang, *J. Am. Chem. Soc.* **123**, 9904 (2001).
- [9] X. Yang, J. Ni, *Phys. Rev. B* **72**, 195426 (2005).
- [10] D. F. Perepichka, F. Rosei, *Silicon nanotubes*, *Small* **2**, 22 (2006).
- [11] E. Durgun, S. Ciraci, *Turk. J. Phys.* **29**, 307 (2005).
- [12] V. Schmidt, J. V. Wittemann, S. Senz, U. Gosele, *Adv. Mater.* **21**, 2681 (2009).
- [13] M. Zhou, R. Li, J. Zhou, X. Guo, B. Liu, Z. Zhang, E. Xie, *J Appl Phys* **106**, 124315 (2009).
- [14] S. B. Fagan, R. J. Baierle, R. Mota, A. J. R. da Silva, A. Fazzio, *Phys. Rev. B* **61**, 9994 (2000).
- [15] S. B. Fagan, R. Mota, R. J. Baierle, G. Paiva, A. J. R. da Silva, A. Fazzio, *J. Mol. Struct. Theochem.* **539**, 101 (2000).
- [16] B. N. Mbenkum, A. S. Schneider, G. Schutz, C. Xu, G. Richter, P. A. van Aken, G. Majer, J. P. Spatz, *ACS Nano* **4**, 1805 (2010).
- [17] S. Hofmann, C. Ducati, R. J. Neill, S. Piscanec, A. C. Ferrari, J. Geng, R. E. Dunin-Borkowski, J. Robertson, *J. Appl. Phys.* **94**, 6005 (2003).
- [18] H. Dai, A. G. Rinzler, P. Nikolaev, A. Thess, D. T. Colbert, R. E. Smalley, *Chem. Phys. Lett.* **260**, 471 (1996).
- [19] J. Gavillet, A. Loiseau, C. Journet, F. Willaime, F. Ducastelle, J. C. Charlier, *Phys. Rev. Lett.* **87**, 275504 (2001).
- [20] S. B. Sinnott, R. Andrews, D. Qian, A. M. Rao, Z. Mao, E. C. Dickey, F. Derbyshire, *Chem. Phys. Lett.* **315**, 25 (1999).
- [21] R. T. K. Baker, M. A. Barber, P. S. Harris, F. S. Feates, R. J. Waite, *J. Catal.* **26**, 51 (1972).
- [22] R. T. K. Baker, P. S. Harris, R. B. Thomas, R. J. Waite, *J. Catal.* **30**, 86 (1973).
- [23] N. M. Rodriguez, *J. Mater Res.* **8**, 3233 (1993).
- [24] R. T. K. Baker, *Carbon* **27**, 315 (1989).
- [25] M. Saeidi, *J. Cryst. Growth* **404**, 34(2014).
- [26] M. Saeidi, *Iranian J. Sci. Tech. Trans. A* **39**, 1 (2015).
- [27] M. Saeidi, M. Vaezzadeh, *Curr. Nanosci.* **5**, 302 (2009).
- [28] M. Saeidi, M. Vaezzadeh, *Physica E* **41**, 1723 (2009).
- [29] M. Saeidi, M. Vaezzadeh, *Iranian J. Sci. Tech. Trans.* **A1**, 29 (2011).
- [30] H. Shahrokhbadi, M. Saeidi, M. Vaezzadeh, H. Shahivandi, M. Salehian, *J. Cryst. Growth* **371**, 56 (2013).
- [31] M. Saeidi, *Physica E* **70**, 225 (2015).
- [32] M. Saeidi, M. Vaezzadeh, F. Badakhshan, *Physica B* **406**, 1038 (2011).
- [33] M. Saeidi, M. Vaezzadeh, M. Mansouri, *J. Cryst. Growth* **345**, 7 (2012).

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