

FORMATION OF FOREST OF SINGLE-WALLED CARBON NANOTUBES IN PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION

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A surface diffusion model, describing the growth of forest of single-walled carbon nanotubes in plasma-enhanced chemical vapor deposition, is developed. Using this model, the growth rates of the nanotubes and the growth rates of the carbon film between nanotubes on the substrate are determined, as functions of external parameters. The model accounts for nonuniformity of deposition of neutral particles and etching gas atoms on the nanotube surfaces from plasma environment. It was found that at not very large SWCNT length a SWCNT growth rate decreases with increasing the SWCNT length.

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INTRODUCTION

Formation of multiwalled carbon nanotubes and nanofibers in plasma-enhanced chemical vapor deposition (PECVD) has been studied theoretically and experimentally by many authors, while plasma-aided growth of single-walled carbon nanotubes (SWCNTs) is not well-studied [1-5]. SWCNT synthesis at low substrate temperatures still remains a challenge. Progress in effective formation of SWCNTs using PECVD is impossible without understanding processes taking place on the substrate and plasma environment at formation of the nanostructures.

The PECVD growth of SWCNTs was studied theoretically using a surface diffusion model in Ref. [6]. The model proposed in Ref. [6] can be applied only for the case of uniform deposition of neutral particles on the surfaces of the SWCNTs. Meantime, in most of experiments the SWCNTs are grown as a forest, i.e., the distance between individual nanotubes is small ($\sim 1 \mu\text{m}$). As a result, the fluxes of neutral particles on the surfaces of nanotubes are not uniform. The dependence of the fluxes on the distance from the nanotube top can be approximated by an exponential function [7].

We propose a theoretical model describing the growth of SWCNT forest in PECVD. We study SWCNT base growth (i.e., the catalyst particles stay anchored to the substrate) accounting for deposition of hydrocarbon neutrals, ions and the particles of the etching gas, on and between the SWCNTs. The model accounts for nonuniform deposition of neutrals on the surfaces of the SWCNTs.

1. THEORETICAL MODEL

Let us consider close-ended growth of forest of single-walled carbon nanotubes in a plasma environment. The catalyst particles stay anchored to the substrate and the nanotubes have semi-spherical peaks (Fig. 1 of Ref. [6]). The SWCNTs are directed along x -axis and are of the same length L_{NT} . The plasma (created in a $\text{C}_2\text{H}_2/\text{H}_2$ gas discharge) is located above the nanotubes and is the source of various carbon- and hydrogen-bearing neutrals and ions. We assume that the main particles interacting with the surfaces of the SWCNTs and with the substrate surface between the

SWCNTs are the hydrocarbon neutrals C_2H_2 , the hydrocarbon ions C_2H_2^+ and the etching gas atoms H. It is assumed that the distance between the SWCNTs is small, and there is an exponential decay of neutral fluxes on the surfaces of the SWCNTs [7]. We assume that the fluxes of C_2H_2 and H₂ on the surfaces of the SWCNTs are proportional to $\exp(-x/l^*)$, where x is the distance from the top of a nanotube, and l^* is the characteristic decay length. The ions deposit uniformly on the SWCNT surfaces. The adsorption and desorption fluxes of the neutrals are: $j_{ads}=j_a(1-\theta_l)$ and $j_{des}=\theta_a\nu_0\exp(-E_a/k_bT_s)$, where ν_0 is the number of adsorption sites per unit area, $\alpha=\text{CH}$ and H denote C_2H_2 and H neutrals, respectively. $j_a=n_a\nu_{tha}\exp(-x/l^*)/4$ is the flux density of impinging neutral particles. $\nu_{tha}=\sqrt{8k_bT_s}/\pi m_a$ is the thermal velocity, k_b is the Boltzmann constant, $E_a=1,8 \text{ eV}$ is the adsorption energy. n_a , θ_a and m_a are the plasma bulk density, surface coverage, and mass of species α . We suppose that the SWCNT surfaces and the surface between nanotubes are covered by C_2H_2 molecules, C and H atoms. The total surface coverage by the particles is $\theta_a=\theta_{CH}+\theta_H+\theta_C$. Carbon atoms can appear on the SWCNT surfaces by such reactions as thermal dissociation, ion bombardment of adsorbed C_2H_2 molecules and decomposition of C_2H_2^+ ions. The reactions describing the loss of carbon atoms from the SWCNT surfaces are presented in Ref. [6].

The differential equation for the surface density of carbon atoms n_C on the SWCNT surfaces [8]:

$$D_s \frac{d^2 n_C}{dx^2} + Q_C - \frac{n_C}{\tau_a} = 0, \quad (1)$$

where $D_s = a_0^2 \nu \exp(-\delta E_d / k_b T_s)$ is the surface diffusion coefficient of carbon atoms on the SWCNT surfaces, $a_0=0,14 \text{ nm}$ is the interatomic distance in the nanotube, δE_d is the threshold energy of surface diffusion for carbon on a SWCNT surface, $\nu \approx 10^{13} \text{ Hz}$ is the thermal vibration frequency, T_s is the SWCNT surface temperature, $Q_C=2(C_I+j_i)$ is the effective carbon flux to the SWCNT surfaces,

$$C_1 = (v_0 \nu \exp(-\frac{\delta E_i}{k_b T_s}) + j_i \gamma_d) / \left[1 + \frac{2M + L \frac{j_C}{j_{CH}}}{K} + \frac{L}{j_{CH}} \right]$$

$$\tau_a = \left[\nu \exp(-\frac{E_{ev}}{k_b T_s}) + \sigma_{ads} j_H + \frac{2C_1}{v_0} \right]^{-1}$$
 is the time

characterizing carbon loss, j_i is the ion flux, $\sigma_{ads} = 6.8 \times 10^{-16} \text{ cm}^2$ is the cross section of the adsorbed-layer reaction, $\delta E_{ev} = 1.8 \text{ eV}$ is the evaporation energy, $\delta E_i = 2.1 \text{ eV}$ is the activation energy of thermal dissociation,

$$M = v_0 \nu \exp(-\frac{E_a}{k_b T_s}),$$

$$L = v_0 \nu \exp(-\frac{E_a}{k_b T_s}) + v_0 \nu \exp(-\frac{\delta E_i}{k_b T_s}) + v_0 \sigma_{ads} j_H + j_i \gamma_d,$$

$$K = v_0 \nu \exp(-\frac{E_a}{k_b T_s}) + v_0 \sigma_{ads} j_H, \quad \gamma_d = E_i / \delta E_i$$

The Eq(1). should be accompanied by boundary conditions. We assume that [6] :

$$\begin{cases} \frac{\partial}{\partial x} n_C \Big|_{x=0} = 0, \\ -D_s \frac{\partial}{\partial x} n_C = k n_C \Big|_{x=L_{NT}}, \end{cases} \quad (2)$$

where $k = a_0 \nu \exp(-\frac{\delta E_{inc}}{k_b T_s})$, δE_{inc} is the energy of atom

incorporation into the SWCNT wall. The SWCNT growth rate is [6]:

$$V_{NT} = \frac{dL_{NT}}{dt} = -\Omega D_s \frac{dn_c}{dx} \Big|_{x=L_{NT}}, \quad (3)$$

where Ω is the area per unit C atom in a SWCNT wall.

Ions and neutral particles deposit also between nanotubes. Their deposition may be accompanied by formation of carbon film. The film formation is affected by the processes presented in Ref. [6].

The rate of carbon film deposition at $x=L_{NT}$ is determined by the flux

$$j_{dep} \approx n_C \nu \exp(-\delta E_f / k_b T_s) + j_i \theta_{CH} \gamma_s + j_i - \frac{1}{4} (1 - \theta_i) \nu_0 \sigma_{bulk} j_H - j_i (1 - \theta_i) \gamma_{sp},$$

where δE_f is the activation energy of carbon incorporation into the film, $\sigma_{bulk} \approx 6.8 \times 10^{15}$ is the cross section for the reaction of etching, γ_{sp} is the sputtering yield [6].

The growth rate of carbon film is

$$V_{dep} = \frac{\partial}{\partial t} L_{dep} = j_{dep} M_{dep} / \rho N_a, \quad (4)$$

where L_{dep} is the film width, N_a is the Avogadro number, ρ is the film density, and M_{dep} is the mole mass of the growing film material.

2. RESULTS

The system of Eqs. (2) was solved. Using the obtained solution of Eqs. (2), the growth rates of the SWCNTs V_{NT} and of the carbon film V_{dep} were calculated from Eqs. (3) and (4) for different external conditions. In Fig.1(a), the SWCNT growth rates are

shown as functions of the SWNT length. The curves in Fig.1(a) are obtained for $T_s = 1000 \text{ K}$, $l^* = 2.5 \mu\text{m}$, $n_i = 10^{10} \text{ cm}^{-3}$, $j_H = 10^{-3} j_{CH}$, $E_i = 2.1 \text{ eV}$. The averaged hydrocarbon flux on the SWCNT surfaces j_{CH} is taken to be $2.25 \times 10^{-19} \text{ cm}^{-2} \text{ s}^{-1}$

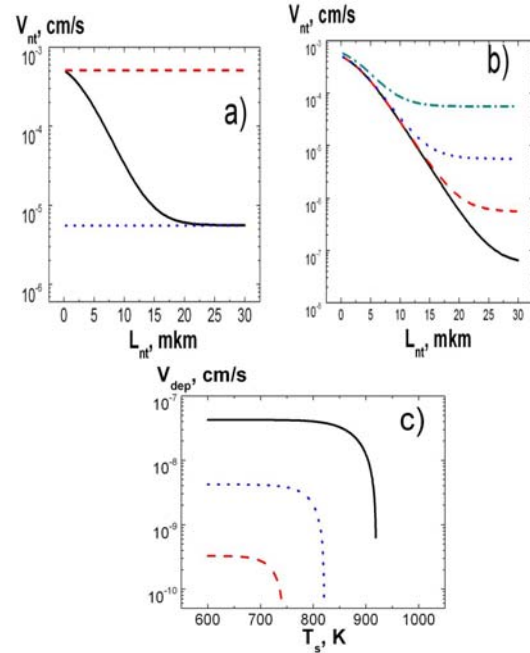


Fig. 1. The SWCNT growth rates as functions of the SWCNT length in the nonuniform and uniform cases (a); the SWCNT growth rate (b) and the growth rate of the film between the SWCNTs (c) in the nonuniform case for different n_i .

The solid curve in Fig.1,a corresponds to the case of nonuniform fluxes of neutral particles on the surfaces of the SWCNTs (“nonuniform” case), while the dashed curve is obtained assuming that the fluxes of C_2H_2 and H on the SWCNT surfaces are independent on x -coordinate (“uniform” case). The dotted curve in Fig.1(a) is obtained assuming that only the ions C_2H_2^+ deposit on the surfaces of the SWCNTs and the neutral particles fluxes are absent.

At small SWCNT length the growth rate V_{NT} on L_{NT} in the case of nonuniform fluxes j_{CH} and j_H is nearly the same as that obtained for the case when the fluxes j_{CH} and j_H do not depend on x -coordinate (Fig. 1,a). At $L_{NT} > 2 \mu\text{m}$, the growth rates obtained in the nonuniform case are smaller than those corresponding to the uniform case. The difference is due to decrease of the hydrocarbon flux on the SWCNT surfaces at $x=L_{NT}$ with increasing the SWCNT length in the nonuniform case. At large nanotube length ($> 22 \mu\text{m}$), the flux j_{CH} at $x=L_{NT}$ in the nonuniform case is very small, and the growth rate is nearly the same as that calculated for the case when only the ions C_2H_2^+ deposit on the SWCNT surfaces. In the range $2 \mu\text{m} < L_{NT} < 22 \mu\text{m}$, the growth rate in the nonuniform case is decreasing with L_{NT} increase due to decrease of the flux j_{CH} at $x=L_{NT}$.

In Fig. 1,b, the SWCNT growth rates are shown as functions of the SWNT length for different ion densities: 10^8 cm^{-3} (dashed curve), 10^9 cm^{-3} (dotted curve), 10^{10} cm^{-3} (solid curve). The curves in Fig.1(b) are obtained for $T_s = 1000 \text{ K}$, $l^* = 2.5 \mu\text{m}$, $j_{CH} = 2.25 \times 10^{-19} \text{ cm}^{-2} \text{ s}^{-1}$, $j_H = 10^{-3} j_{CH}$, $E_i = 2.1 \text{ eV}$. It is seen from Fig. 1,b that at relatively large $L_{NT} (> 20 \mu\text{m})$ the SWCNT growth rate increases with an increase of ion

density due to enhancement of production of carbon atoms in ion-induced processes.

Formation of single-walled carbon nanotubes, when the catalyst particles are attached to the substrate, is possible only at absence of a carbon film between the catalyst particles. Fig.1(c) shows the dependence of growth rate of the carbon film on T_s for different ion densities: 10^8 cm^{-3} (dashed curve), 10^9 cm^{-3} (dotted curve), 10^{10} cm^{-3} (solid curve). The curves in Fig.1(c) are obtained for $L_{NT}=5 \text{ }\mu\text{m}$, $l^*=2,5 \text{ }\mu\text{m}$, $j_H=10^{-3}j_{CH}$, $j_{CH}=2,25 \times 10^{-19} \text{ cm}^{-2} \text{ s}^{-1}$. One can see that the growth rate V_{dep} increases with an increase of ion density. This is due to enhancement of ion-induced stitching of C_2H_2 and direct incorporation of C_2H_2^+ ions. At large surface temperatures ($T_s > 900 \text{ K}$), the carbon film between the nanotubes is absent due to evaporation of carbon particles from the substrate.

CONCLUSIONS

In conclusions, a surface diffusion model, describing the growth of forest of vertically-aligned SWCNTs in PECVD and accounting for the nonuniformity of flux of neutral particles on the surfaces of the SWCNTs is developed. At not very large SWCNT length ($< 20 \text{ }\mu\text{m}$), the SWCNT growth rate decreases with increasing the SWCNT length. At large $L_{NT} (> 20 \text{ }\mu\text{m})$, the growth rate slightly depends on L_{NT} and approximately equals to that corresponding to the case when only hydrocarbon ions deposit on the SWCNT surfaces.

Note, that in our previous paper [8] it was found that the growth rate of the SWCNT forest may increase with increasing L_{NT} . This increase was observed for relatively low surface temperatures ($\leq 700 \text{ K}$). Meantime, at small T_s , formation of carbon film between the SWCNTs takes place [see Fig.1(c)]. This can eventually stop the SWCNT growth. Similarly to the case of uniform fluxes of neutral particles on the surfaces of the SWCNTs, the growth rate of the SWCNT forest increases with increasing ion flux to the surfaces of the SWCNTs.

The model presented here can be used for optimizing synthesis of SWCNTs and other nanostructures in PECVD [9-10].

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ФОРМИРОВАНИЕ ЛЕСА ОДНОСЛОЙНЫХ УГЛЕРОДНЫХ НАНОТРУБОК ПРИ ПЛАЗМОХИМИЧЕСКОМ ОСАЖДЕНИИ

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Разработано поверхностную диффузионную модель, описывающую рост леса однослойных углеродных нанотрубок при плазмохимическом осаждении из газовой фазы. С помощью данной модели были определены скорости роста нанотрубок и скорости роста углеродной плёнки между нанотрубками, как функции внешних параметров. Модель учитывает неоднородность осаждения частиц на поверхность нанотрубки. Показано, что скорость роста нанотрубок падает при увеличении их длины при малых длинах.

ФОРМУВАННЯ ЛІСУ ОДНОШАРОВИХ ВУГЛЕЦЕВИХ НАНОТРУБОК ПРИ ПЛАЗМОХІМІЧНОМУ ОСАДЖЕННІ

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Розроблено поверхневу дифузійну модель, яка описує ріст лісу одношарових вуглецевих нанотрубок при плазмохімічному осадженні з газової фази. За допомогою цієї моделі було визначено швидкості зростання нанотрубок та швидкості зростання вуглецевої плівки між нанотрубками, як функції зовнішніх параметрів. Модель враховує неоднорідність осадження частинок на поверхню нанотрубки. Показано, що швидкість зростання нанотрубок зменшується із збільшенням їх довжини при малих довжинах.