GROWTH OF FOREST OF SINGLE-WALLED CARBON NANOTUBES AT INHOMOGENIOUS FLUXES FROM PLASMA

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The growth of forest of single-walled carbon nanotubes (SWCNTs) in plasma-enhanced chemical vapor deposition (PECVD) is studied using a deposition model. The inhomogeneity in deposition of neutrals from plasma on the SWCNTs, which is typical for growth of the nanostructures in PECVD, is accounted for. It is investigated how the growth rate and the residence time of carbon atoms on SWCNT surfaces depend on the SWCNT length and the decay length characterizing deposition of neutral fluxes on the SWCNTs. The obtained results can be used for optimizing the synthesis of related nanoassembles in low-temperature plasma-assisted nanofabrication.

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INTRODUCTION

Plasma-enhanced chemical vapor deposition (PECVD) techniques have been successfully used for production of different nanoscale materials including carbon nanofibers (CNFs) and carbon nanotubes (CNTs) [1, 2]. These carbon nanostructures, formed by PECVD, have better alignment and can be grown at higher deposition rates and lower substrate temperatures than those synthesized by thermal chemical vapor deposition (CVD) or other methods.

In this paper, we study formation of a SWCNT forest in plasma, using a deposition model, that is based on mass balance equations for adsorbed species on the single-walled carbon nanotube (SWCNT) surfaces. This model is an extension of the model previously used for description of the growth of an isolated SWCNT, where it was assumed that plasma particles were deposited homogeneously on the surfaces of SWCNTs [3]. We account for the inhomogeneity in deposition of neutrals from plasma on the SWCNTs. The model equations are solved using the WKB (Wentzel-Kramers-Brillouin) approach, and an analytical expression for the growth rate of the SWCNT forest is obtained as a function of parameters of the SWCNTs and ion and neutral fluxes. We investigate how the growth rate depends on the SWCNT length and the decay length characterizing the deposition of neutral fluxes on the SWCNTs.

1. THEORETICAL MODEL

Let us consider close-ended growth of a forest of SWCNTs with semi-spherical peaks. It is assumed that the SWCNTs have the same length, and the catalyst nanoparticles are anchored to the base (at $x=L_{NT}$, where x is the coordinate along the SWCNT axis and L_{NT} is the length) of a SWCNT. The plasma produced in a C_2H_2/H_2 gas discharge is located above the forest of SWCNTs, and the main particles which interact with surfaces of the SWCNTs are hydrocarbon neutrals (C_2H_2), hydrocarbon ions ($C_2H_2^+$) and atoms or molecules of an etching gas (atomic hydrogen H). The hydrocarbon neutrals and atomic hydrogen are adsorbed and desorbed on the SWCNT surfaces as well as on the substrate surface between the SWCNTs. We consider the case when the distance between the SWCNTs is small (≤1 μm), and, therefore, it is assumed that the fluxes of neutral particles onto the surfaces of the SWCNTs decrease exponentially ($exp(-x/l^*)$, where x is the distance from the top of a nanotube, and l^* is the characteristic decay length [4].

The adsorption and desorption fluxes of the neutrals can be presented as: $j_{\alpha ads}=j_\alpha(1-\theta_t)$ and $j_{\alpha des}=\theta_a \upsilon_0 \nu \times \times exp(-E_a/k_bT_s)$, where υ_0 is the number of adsorption sites per unit area, α=CH and H denote C_2H_2 and H neutrals, respectively; $j_\alpha=n_a\upsilon_{tha}\nu exp(-x/l^*)/4$ is the flux density of impinging neutral particles; T_s is the SWCNT surface temperature; $\upsilon_{tha}=\sqrt{8k_bT_s/\pi m_a}$ is the thermal velocity, k_b is the Boltzmann constant, E_a is the adsorption energy; n_a, θ_a and m_a are the plasma bulk density, surface coverage, and mass of species α. The ion flux is determined as $j_i \sim n_i\sqrt{T_e/m_i}$, where T_e is the plasma electron temperature, and n_i and m_i are the ion density and mass, respectively. Since ions have essentially larger energies than neutrals, it is assumed that ions are deposited homogeneously on the SWCNT surfaces [5].

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 $\theta_t=\theta_{CH}+\theta_H+\theta_C$. Carbon atoms can appear on the SWCNT surfaces due to such reactions as thermal dissociation, ion bombardment of adsorbed C_2H_2 molecules and decomposition of C_2H_2+ ions.

We obtain the differential equation for the surface density of carbon atoms n_C on the SWCNT surfaces:

$$D_s d^2 n_c / dx^2 + Q_C - n_C/\tau_a = 0, \qquad (1)$$

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 nm is the interatomic distance in the nanotube, δE_d is the threshold energy of surface diffusion for carbon on a SWCNT surface, $\nu \approx 10^{13}$ Hz is the thermal vibration frequency, $Q_C=2(C_1+j_i)$ is the effective carbon flux to the SWCNT surfaces,

$$C_1 = \frac{\upsilon_0 \nu \exp(-\delta E_i / k_b T_s) + j_i}{1 + (2M + L j_H / j_{CH})/K + L/j_{CH}},$$

$\tau_a = \left[\nu \exp(-\frac{E_{ev}}{k_b T_s}) + \sigma_{ads} j_H + \frac{2C_1}{\nu_0} \right]^{-1}$ is the time characterizing the carbon loss, σ_{ads}=6.8×10^{-16} cm^2 is the cross section of the adsorbed-layer reaction, E_{ev}=1.8 eV is the evaporation energy for carbon atoms, δE_i=2.1 eV is the activation energy of thermal dissociation, $M = \upsilon_0 \nu \exp(-\frac{\delta E_i}{k_b T_s})$,

$$L = \upsilon_0 \nu \exp(-\frac{E_a}{k_b T_s}) + \upsilon_0 \nu \exp(-\frac{\delta E_i}{k_b T_s}) + \upsilon_0 \sigma_{ads} j_H + j_i,$$

$$K = \upsilon_0 \nu \exp(-\frac{E_a}{k_b T_s}) + \upsilon_0 \sigma_{ads} j_H.$$

Eq. (1) should be accompanied by boundary conditions. We assume that:

$$\frac{\partial}{\partial x} n_C \Big|_{x=0} = 0, \qquad -D_s \frac{\partial}{\partial x} n_C = k n_C \Big|_{x=L_{NT}}, \tag{2}$$

where $k = a_0 \nu \exp(-\delta E_{inc} / k_b T_s)$, δE_{inc} is the energy of atom incorporation into the SWCNT wall.

In general, Eq. (1) cannot be solved analytically. However, when the variation of the fluxes of neutrals and ions along the SWCNTs is weak, the solution of Eq. (1) can be found using the WKB approach. If the surface diffusion length is smaller than l^*, the SWCNT growth rate is:

$$V_{NT} = -\Omega D_S \frac{dn_c}{dx} \Big|_{x=L_{NT}} = \frac{k \Omega Q_{C1} \tau_{a1} \sinh(\xi)}{\sinh(\xi) + (k \lambda_{D1} / D_s) \cosh(\xi)}, \tag{3}$$

where Ω is the area per unit C atom in a SWCNT wall, $\lambda_{D1} = \sqrt{D_s \tau_{a1}}$ is the surface diffusion length at $x=L_{NT}$ and $\xi = \int_0^{L_{NT}} (1/\lambda_D) dx$, $\tau_{a1}=\tau_a(x=L_{NT})$.

Ions and neutral particles are deposited also between nanotubes. Their deposition can be accompanied by formation of carbon film. The film formation between SWCNTs was studied in [3]. Here, we consider such nanotube's and plasma parameters when formation of the film between nanotubes does not take place.

RESULTS

Using the analytical results presented in the previous section, let analyze how the parameters which characterize the growth of SWCNT forest [the nanostructure growth rate (V_{NT}) and the time characterizing the carbon loss near the nanotube base (τ_{a1})] depend on the SWCNT length, the decay length characterizing the deposition of neutrals on the nanotube surfaces, and the substrate temperature. To make this analysis, we vary the SWCNT length, the decay lengths for neutral fluxes, as well as the substrate temperature in our calculations, and then observe how these changes affect the SWCNT growth parameters.

The growth rate of SWCNTs V_{NT} is calculated from Eq. (3) for different external conditions. In Figs. 1 and 2, the SWCNT growth rate V_{NT} and the characteristic residence time of carbon atoms τ_{a1} are shown as functions of the SWNT length L_{NT} for different decay lengths of neutral particle fluxes. The dependences are obtained for the SWCNT surface temperatures T_S=800 K (see Fig. 1) and T_S=1000 K (see Fig. 2), assuming that ions are deposited homogeneously on the nanotubes. One can see from Fig. 1,a that at low temperatures the SWCNT growth rate V_{NT} first increases with increase of the length L_{NT}, reaching a maximum at a certain length, and then it decreases. At larger l^*, the maximum is observed for larger lengths. For long nanotubes, the growth rate depends slightly on the SWCNT length.

For nanotubes with the length in the range between $6l^*$ and $10l^*$, the effective carbon flux to the nanotube base decreases with an increase of L_{NT} because of the exponential dependence of the hydrocarbon flux on the coordinate. At large lengths (>10 l^*), the neutral particle fluxes to the nanotube's base are small, and the production of carbon adatoms is mainly due to decomposition of ions on the SWCNT surfaces. As a result, for these lengths, the effective carbon flux and the SWCNT growth rate are nearly independent on the length L_{NT}. For L_{NT}>>l*, the residence time also depends slightly on the SWCNT length (see Fig. 1,b) because for large L_{NT} the loss of carbon atoms near a nanotube base is mainly due to their evaporation.

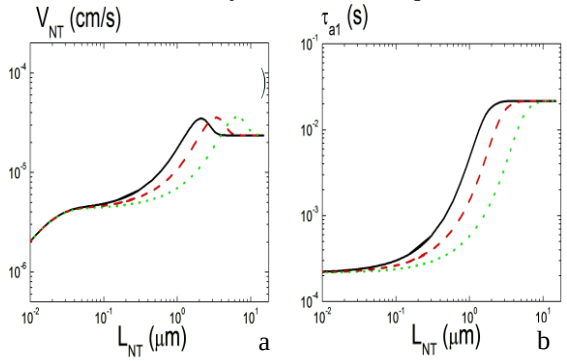

Fig. 1. Dependences of the SWCNT growth rate (a) and time characterizing the carbon loss (b) on the nanotube's length L_{NT}. The external parameters for (a) and (b) are T_S=800 K, n_{CH}=10^{15} cm^{-3}, n_i=10^{10} cm^{-3}, j_H=0.3j_{CH}, and l^*=1.0 (dotted line), l^*=0. μm (dashed line), l^*=0.3 μm (solid line)

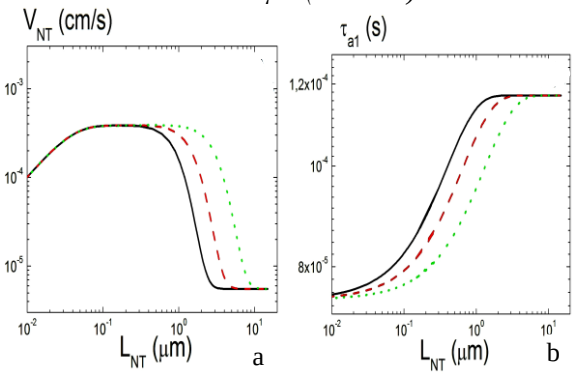

Fig. 2. The same as in Fig. 1, but for T_S=1000 K

Due to decrease of the loss of carbon atoms, the residence time τ_{a1} becomes larger with increasing L_{NT} (see Fig. 1,b). At low T_s, the effect of etching gas on processes on the SWCNT surfaces is essential, and the difference in the residence times for small and large nanotube lengths is very large (~ 100 times (see Fig. 1,b)). Due to increase of τ_{a1}, the growth rate becomes larger with increasing L_{NT} for small SWCNT

lengths. For nanotubes of middle length ($6l^* < L_{NT} < 10l^*$), the growth rate decreases with the length increase because of decrease of Q_C at small variation of the residence time.

For large surface temperatures (see Fig. 2), the effect of etching gas on the loss of carbon adatoms from the SWCNT surfaces is less pronounced and thermal effects are more important. The difference in τ_{a1} for small and large L_{NT} is small (see Fig. 2,b), comparing with this difference for lower T_S. For small L_{NT}, V_{NT} increases with an increase of L_{NT}. For $0.1\mu m < L_{NT} < l^*$, Q_C decrease is accompanied by an increase of τ_{a1} and the growth rate depends slightly on L_{NT} (see Fig. 2,a). For $l^* < L_{NT} < 10l^*$, V_{NT} decreases due to the decrease of Q_C. For large nanotube's lengths, the fluxes of neutral particles to the nanotube's base are small, and the growth rate is a function only of the ion flux.

CONCLUSIONS

The theoretical model, describing the growth of a SWCNT forest in PECVD, is developed. Using this model, it is shown that the dependence for the growth rate of the SWCNT forest on the nanotube's length at nonuniform deposition of neutrals on the surfaces of the SWCNTs can be different from that in the case of their uniform deposition. In the case of uniform deposition, the growth rate becomes larger with an increase of L_{NT}, until it reaches a maximum (at $L_{NT} \sim 0.1$ μm in [4]), and V_{NT} is independent on the length for large lengths. At nonuniform deposition of neutrals and uniform deposition of ions, the growth rate first becomes larger with an increase of L_{NT} for small lengths, reaches a maximum at a certain length and then decreases, until it reaches the magnitude, corresponding to the case, when only ions are deposited on the nanostructures (see Fig. 1,a). For long nanotubes, the loss of carbon atoms near the SWCNT base is mainly due to evaporation. As a result, the residence time of carbon atoms at $x = L_{NT}$ is larger for long nanotubes than for short SWCNTs (see Figs. 1,b and 2,b). Since the evaporation is more intensive at large surface temperatures, the growth rate of long nanotubes may increase with decreasing the SWCNT surface temperature (Figs. 1,a and 2,a).

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РОСТ ЛЕСА ОДНОСЛОЙНЫХ УГЛЕРОДНЫХ НАНОТРУБОК ПРИ НЕОДНОРОДНЫХ ПОТОКАХ ИЗ ПЛАЗМЫ

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Изучен рост леса однослойных углеродных нанотрубок (ОУНТ) в процессе плазменно-химического осаждения (ПХО) на основе разработанной теоретической модели для описания этого осаждения. При этом учтена неоднородность осаждения нейтральных частиц из плазмы на поверхности ОУНТ, которая характерна для роста этих наноструктур в процессе ПХО. Исследовано, как скорость роста ОУНТ и время жизни атомов углерода на их поверхности зависят от длины ОУНТ и глубины проникновения потока нейтральных частиц в лес ОУНТ. Полученные результаты могут быть использованы для оптимизации синтеза различных наноструктур в низкотемпературной плазме.

РІСТ ЛІСУ ОДНОШАРОВИХ ВУГЛЕЦЕВИХ НАНОТРУБОК ЗА НЕОДНОРІДНИХ ПОТОКІВ ІЗ ПЛАЗМИ

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Вивчено ріст лісу одношарових вуглецевих нанотрубок (ОВНТ) у процесі плазмово-хімічного осадження (ПХО) на основі розробленої теоретичної моделі для опису цього осадження. При цьому враховано неоднорідність осадження нейтральних частинок із плазми на поверхні ОВНТ, яка є характерною для росту цих наноструктур у процесі ПХО. Досліджено, як швидкість росту ОВНТ та час життя атомів вуглецю на їх поверхні залежать від довжини ОВНТ та глибини проникнення потоку нейтральних частинок до лісу ОВНТ. Здобуті результати можуть бути використані для оптимізації синтезу різних наноструктур у низькотемпературній плазмі.