Role of etchant on the morphology of plasma grown carbon nanofibers: Theoretical modeling

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Abstract

The analytical model to study the effect of etching gas flow rate on the final shape of the carbon nanofibers (CNFs) synthesized via plasma enhanced chemical vapor deposition technique (PECVD) is developed. The analytical model developed accounts the plasma sheath effects along with the charging rate of carbon nanofiber surface, kinetics of various plasma species (electrons, positively charged ions and neutrals), and growth rate of carbon nanofibers. The results of this investigation demonstrate that flow rate of etching gas extensively affect the morphology of the carbon nanofibers. It is found that tilt angle of carbon nanofiber increases and tip diameter of carbon nanofiber decreases with increase in etching gas flow rate in the plasma chamber. In addition, we found that base diameter of the carbon nanofiber increases with decrease in flow rate of etching gas. Our theoretical results are in line with experimental observations. The present study can be utilized to synthesize the efficient field emission devices based on carbon nanofibers.

I. Introduction

Controlled growth of carbon nanofibers (CNFs) implies the deterministic (precise) control of their morphology. The shape of nanostructure is an important aspect in realization of practical nanoscale devices [1], such as; CNFs having wide base provides higher mechanical stability. However, much enhanced field emission properties can be obtained from the CNFs having small tip diameters. Amount of etchant species present in the reactive plasma is significant in this regard [2]. In the present paper, we try to model the effect of etching gas flow rate on the morphology of the CNFs.

II. Model

In the present work, the effect of etching gas flow rate on the final morphology of plasma grown carbon nanofiber is examined through the analytical model that accounts the following scenario; (i) the acetylene as carbon source and hydrogen as etching gases, respectively, (ii) the CNF growth on the catalyst nanoparticle placed over silicon substrate, (iii) the plasma consisting

of electrons, ions ($C_2H_2^+$) and neutrals (C_2H_2) of acetylene, ions (H^+) and neutrals (H) of hydrogen denoted type A and B, respectively. (iv) formation of plasma sheath between the bulk plasma and substrate surface, and (v) sheath equations to study the energy and fluxes of plasma species [3]. The main equations of the model considered are:

$$\partial_t(n_j) = \alpha_j n_e n_{ij} - \beta_j n_j + \frac{n_{cnf}}{\lambda_d}(1-\gamma_{ij})\left(I_{ij}+K_{ij}\right) - \frac{n_{cnf}}{\lambda_d}\gamma_j\left(I_j+K_j\right) + F_j - O_j - \sum_{ljj'} k_l n_j n_{j'} + \sum_{pjj'} k_p n_{j'} n_j, \quad (1)$$

where I_{ij}, K_{ij}, I_e, and K_e are the ions and electrons collection currents at the CNF tip and curved surface [4], respectively where j refers to the ions of type A and B. ionization, n_e, n_{ij}, and n_j are the number density of electrons, ions, and neutrals, respectively. λ_d is the sheath width, J_{aij} and J_{dij} are adsorption and desorption flux onto/from catalyst nanoparticle surface, k_l and k_p are the reactions rate coefficients [5]. $F_j\left[=\frac{4.4\times10^{17}\times f_j}{V}\right]$ and $O_j\left(=\frac{R_p\times n_j}{V}\right)$ are the j^{th} species inflow rate and outflow rate into/from the plasma chamber, respectively. f_j is the inflow rate of corresponding gas, $V\left(\approx 2\times10^4\ \mathrm{cm}^3\right)$ is the volume of the chamber, and R_p is the pumping rate [6]. The Eq. (1) refer to the kinetics of neutral atoms in the plasma on account of electron-ion recombination, ionization, neutralization of ions collected at the CNF surface, accretion of neutrals at the CNF surface, inflow and outflow rate of neutral species from plasma chamber, and reactions between ions and neutrals in the plasma as mentioned above.

$$\partial_t\left[\pi\left(D^2-d^2\right)h\right] = \left[\frac{D_S n_C\times\pi D^2}{\upsilon\times\pi D} + \frac{D_b n_C\times\pi D}{2\upsilon} + 4kn_C\times\pi D^2\right]\times\left(\frac{p}{\rho_{cnf} I_{iA}}\right) + J_A\left(1-\theta_t\right) + J_A\exp\left(\frac{-\delta E_{th}}{k_B T_S}\right) + \frac{n_{sj} J_{iB} y_d}{\upsilon_0} + n_{sj}\upsilon\exp\left(\frac{-\delta E_i}{k_B T_S}\right) + J_{iB} - J_B\exp\left(\frac{-E_{aH}}{k_B T_S}\right) + \frac{16 D_m m_{cat}}{\rho_{cat}\times\pi D^2}, \quad (2)$$

where *D*, *d*, and *h* are the CNF base diameter, tip diameter, and height, respectively. n_C is the number of carbon species per unit area [4], n_{sj} are the surface concentration of j^{th} type of atom, k is the incorporation speed of carbon species into the graphene layers, The Eq. (2) represents the growth rate equation of CNF on account of the surface and bulk diffusion of carbon species through the catalyst surface, and incorporation of carbon species in the form of graphene layers around the catalyst nanoparticle. Due to continuous carbon supply, CNF grows in planar as well as vertical direction. The highly reactive hydrogen (H) radical etches the terminal carbons and

saturates the planar CNF growth. Thus, the Eq. (2) also accounts the various processes responsible for etching of CNF such as; adsorption of H atoms on the catalyst surface, incoming flux of H^+ due to thermal dehydrogenation of hydrocarbon ions, ion induced decomposition of hydrogen, flux of hydrogen species due to thermal dissociation of hydrocarbons, direct hydrogen flux due to hydrogen ion decomposition, and desorption of hydrogen species from the catalyst surface, and self-diffusion of metal atom [7].

III. Results and Discussion

The first order differential equations formulated in the present paper has been solved simultaneously for the glow discharge parameters with appropriate boundary conditions i.e., $n_e = 10^{14} cm^{-3}$, $n_{iA0} = 0.3 n_e$, $n_{iB} = 0.7 n_e$, $n_A = 10^{15}\ cm^{-3}$, $n_B = 10^{16}\ cm^{-3}$, substrate temperature T_s (= 500 ^{0}C), $\gamma_e = \gamma_{ij} = \gamma_j = 1$, total surface coverage θ_t =0.001, acetylene flow rate $f_A (= 60\ sccm)$. Since catalyst nanoparticle act as the fundamental nucleation site of CNF, therefore, at the nucleation stage the diameter of the CNF is given by the catalyst nanoparticle which is assumed to be 100 nm.

Fig. 1 shows the time variation of the CNF (a) base diameter and (b) tip diameter as a function of hydrogen gas flow rate. From Fig. 1(a), one can see that CNF base diameter remains almost unchanged with growth time at high hydrogen flow rate (greater than the flow rate of hydrocarbon gas). At high hydrogen content, equilibrium is set up between the etching of the CNF side walls by the hydrogen radicals and carbon deposition rate. However, base diameter begins to increase with decrease in hydrogen flow rate and significant increase can be seen when hydrogen flow rate is below the acetylene flow rate. This is imputable to the fact that carbon deposition rate at the side walls dominates over the CNF etching rate by hydrogen when less hydrogen radicals (or excess hydrocarbon species) are present in the plasma (cf. fig. 2). Moreover, Fig. 1(b) shows that CNF tip diameter decreases with growth time because of the compressive stress exerted by the inclined graphene layers on the catalyst nanoparticle and increases with decrease in hydrogen gas flow rate because number of etching species i.e. hydrogen radicals decreases in the plasma (cf. fig.2).

Fig. 3 shows the variation of tilt angle of graphene layers about the CNF growth axis (α) with the etching gas flow rate (hydrogen gas flow rate). The tilt angle of graphene layers depends on the CNF tip as well as base diameter [4], and both (tip as well as base diameter) decreases with increase in etching gas flow rate. Thus, inclination of graphitic layers about the growth axis

increases with etching gas flow rate. Some of the theoretical findings of the present work are in good agreement with the existing experimental observations of Caughman *et al.* [8] and Merkulov *et al.* [9]. Moreover, the present study can be further extended to study the growth of other carbon nanostructures in the presence of plasma.

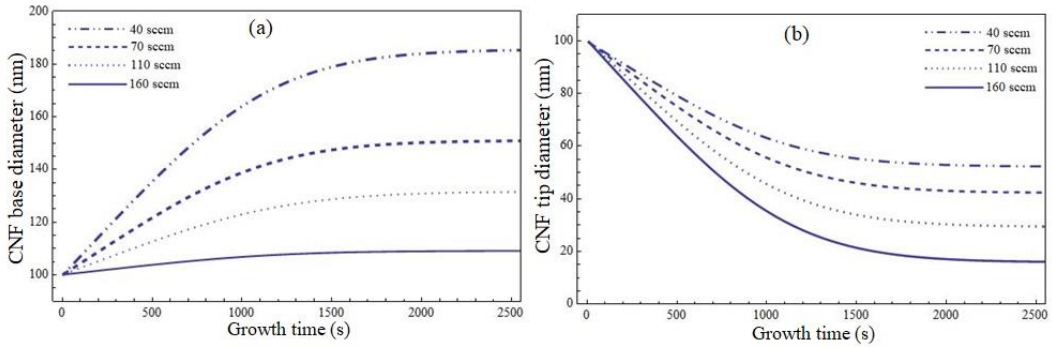

Fig. 1. Time variation of (a) CNF base diameter and (b) CNF tip diameter as a function of etching gas flow rate.

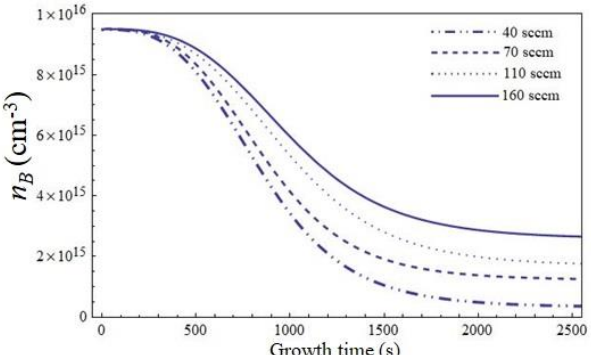

Fig. 2. Time variation of n_B as a function of etching gas flow rate.

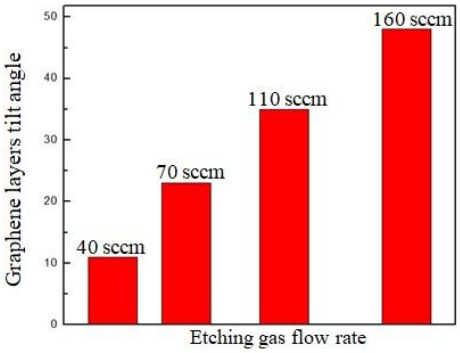

Fig. 3. Variation of graphene layers tilt angle with etching gas flow rate

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