Theoretical Investigations to Study the Effect of C_2H_2/H_2 gas ratio on the Multi-walled Carbon Nanotubes Growth

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ABSTRACT

Carbon Nanotubes are large macromolecules that are unique for their size, shape, and extraordinary physical properties. Their enthralling structures have sparked much interest in recent years and a large expanse of research has been devoted to their understanding. The theoretical model to investigate the effect of acetylene/hydrogen **(**C_2H_2/H_2) gas ratio on the plasma assisted growth of multi-walled carbon nanotubes (MWCNTs) is developed. The present model accounts the charging rate equation of the MWCNTs, kinetics and energy balance equations of all the plasma species, energy balance of MWCNTs, and growth rate of MWCNTs in the reactive plasma composed of Acetylene + Hydrogen + Argon. In our investigations, it is established that the MWCNTs growth rate increases with increase in the acetylene/hydrogen gas ratio. Moreover, it is also found that the diameter of the CNT decreases with decrease in gas ratio.

I. INTRODUCTION

Plasma enhanced chemical vapor deposition (PECVD) has garnered attention than other methods due to the advantages of a highly efficient and vertical growth of nanotubes at low-temperature [1-5]. In PECVD, the main parameters are the growth temperature, growth time, type of substrate, catalyst, the composition of gases used in PECVD, types of feed or reducing or carrier gases and respective flow rates, etc. The effect of various carrier gases such as argon (Ar), hydrogen (H_2), nitrogen (N_2) and ammonia (NH_3) and their flow rates on the growth of CNTs have been experimentally observed [6-9].

Yap *et al.* [6] have studied that the impact of the addition of different gases to the carbon source gas and found that addition of argon dilutes C_2H_2 and hence reduces the number of molecules reacting. Also, the addition of H_2, as well as N_2, reduces the growth density of MWCNTs. Kayastha *et al.* [7] modified the growth of MWCNTs by the addition of specific carrier gases. On adding argon to acetylene, the growth density was increased and adding H_2 and N_2 decreases the growth density of MWCNTs. Toussi *et al.* [8] investigated different flow rates of Ar carrier gas and found that on increasing the flow rate the yield of CNTs was increased.

In the present study, we try to reason as to why different carrier gases have the observed effects on growth of CNTs. In Sec. II, we have developed a theoretical model consisting of the charging rate equation of CNT, kinetics of all the plasma species, and growth rate of CNT in reactive plasma to study the effect of C_2H_2/H_2 gas ratio on the multi-walled CNTs growth. The outcomes of the study have been discussed in Sec. III and finally, the study is concluded in Sec. IV.

II. MODEL

Following Sodha *et al.* [9], we have considered a reactive plasma composed of acetylene (C_2H_2), hydrogen (H_2) and argon (Ar). The reactive plasma consists of electrons, neutrals and ions of acetylene (type A) and hydrogen (type B) in the present study. For simplicity of the problem, the average radius of multi-walled nanotubes has been considered.

A. Balance equation for electron density in plasma

$$\frac{dn_e}{d\tau} = \left(\beta_A n_A + \beta_B n_B\right) - \left(\alpha_A n_e n_{iA} + \alpha_B n_e n_{iB}\right) - \gamma_e n_{ct} n_{ect}, \quad (1)$$

where β_j and α_j represents the neutral atom ionization coefficient and the ions-electrons recombination coefficient, respectively. The Eq. (1) incorporates the rise in rate of density of electrons due to neutral atom ionization (first term) and the decline due to recombination of electron and ions (second term), and collection current of electrons at the CNT surface (third term).

B. Balance equation for ion density in plasma

$$\frac{dn_{iA}}{d\tau} = \beta_A n_A - \alpha_A n_e n_{iA} - n_{ct} n_{iAct}, \quad (2)$$

$$\frac{dn_{iB}}{d\tau} = \beta_B n_B - \alpha_B n_e n_{iB} - n_{ct} n_{iBct}, \quad (3)$$

The Eqs. (2) and (3) incorporates the rise in rate of density of ions due to neutral atom ionization (first term) and the decline due to recombination of electrons and ions (second term), and collection current of ions (i.e., n_{ijct}) at the CNT surface (third term).

C. Balance equation for neutral atom density in plasma

$$\frac{dn_A}{d\tau} = \alpha_A n_e n_{iA} - \beta_A n_A + n_{ct}\left(1-\gamma_{iA}\right) n_{iAct} - n_{ct}\gamma_A n_{Act}, \quad (4)$$

$$\frac{dn_B}{d\tau} = \alpha_B n_e n_{iB} - \beta_B n_B + n_{ct} n_{iBct}, \quad (5)$$

The Eqs. (4) and (5) incorporates the rise in rate of density neutrals due to recombination of electrons and ions (first term), decline due to ionization (second term), and rise due to the neutrals collected because of neutralization at the CNT surface (third term). The extra term in the Eqs. (4) is due to the deposition of type A neutrals (i.e., n_{jct}) at the CNT surface.

D. Mass Balance equation of CNT

$$\frac{dm_{ct}}{d\tau} = \left(m_A \gamma_A n_{Act} + m_{iA} \gamma_{iA} n_{iAct} \right), \qquad (6)$$

where $m_{ct} = \frac{4}{3}\pi a^3 \rho_{ct}$ represents the CNT mass and ρ_{ct} represents the CNT density. The Eq. (6) represents the rise in the CNT mass density due accretion of neutrals and ions of A type species.

III. RESULTS AND DISCUSSION

We have solved the above stated equations along with others simultaneously cited in the work of Sodha *et al.* [9] for the kinetics and energy balance of all the plasma species and charging of CNT. Keeping hydrocarbon density constant, we are changing the C_2H_2/H_2 gas ratio by varying the hydrogen neutral atom density.

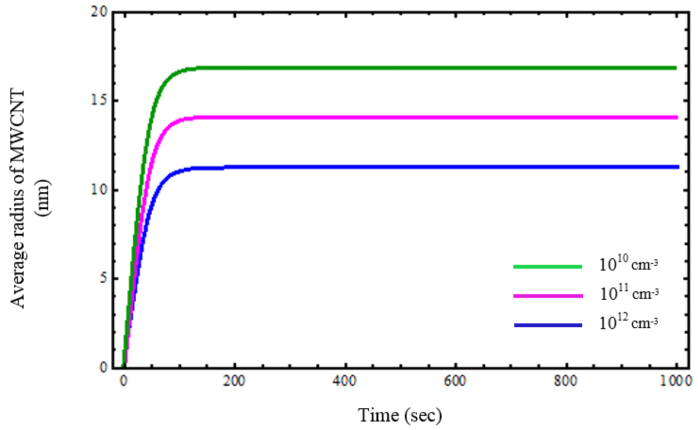

Figure 1. Temporal behaviour of average radius of MWCNTs for different C_2H_2/H_2 gas ratios.

Figure 1 illustrates the temporal behaviour of the average radius of MWCNTs for varying C_2H_2/H_2 gas ratios. It is observed that with time, the average radius of the CNT initially increases and then acquires saturation. The figure also indicates the decline in the average radius with the increasing hydrogen neutral atom density, i.e., the decreasing gas ratio.

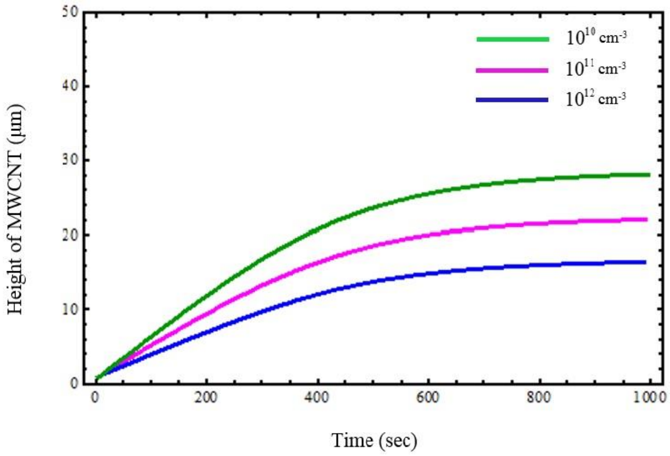

Figure 2. Temporal behaviour of height of MWCNTs for different C_2H_2/H_2 gas ratios.

Figure 2 illustrates temporal behaviour of the height of MWCNTs for varying C_2H_2/H_2 gas ratios. It can be seen that with the increase in hydrogen neutral atom density with time, the height of the CNT and thereby the growth rate increases with the decrease in hydrogen neutral atom density, i.e., the increasing gas ratio.

With the decreasing gas ratio, the nanotubes of lesser radius and height were produced because H_2 dilutes C_2H_2 thereby reducing its concentration, which reduces the hydrocarbon density.

IV. CONCLUSION

It is evaluated from our study that on decreasing the acetylene/hydrogen (C_2H_2/H_2) gas ratio, the growth rate of the MWCNT decreases. The MWCNTs dimensions also declines with the decrease in gas ratio. The field emission characteristics of MWCNT based emitters can be analyzed better from the obtained results of the study.

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