IOP Conf. Series: Journal of Physics: Conf. Series **836** (2017) 012017 doi:10.1088/1742-6596/836/1/012017

Analytical modeling to study the effect of hydrogen plasma on the growth of multi-walled carbon nanotubes

U Sharma[a], N Gupta, R Gupta[1]and S C Sharma

Department of Applied Physics, Delhi Technological University, Delhi-110042, India

Email: [a)]umangsharma2810@gmail.com

Abstract. An analytical model has been developed to study the effect of hydrogen plasma on the growth of Multi-walled Carbon Nanotubes (MWCNTs). The model incorporates the charging rate of the MWCNT, kinetics of plasma species, namely, electrons, positively charged ions, and neutral atoms, growth rate of MWCNT in the presence of CH_4/H_2 plasma. Numerical calculations have been carried out to study the influence of hydrogen number density on the dimensions of MWCNT for typical glow discharge plasma parameters. The impact of hydrogen on the hydrocarbon density has also been studied in the present investigation. The present work can serve as a major tool in better understanding of highly proficient field emitters based on MWCNTs.

1. Introduction

The carbon nanotube (CNT) is a novel carbon structure found since 1991 [1]. CNTs due to their extraordinary mechanical properties, have been getting much attention for a wide variety of applications. Maruyama et al. [2] prospered in producing high-purity single-walled CNTs (SWCNTs) with a high number density. Hata et al. [3] discovered a way to grow high-purity SWCNTs with a high growth rate by adding a small amount of H_2O vapor to the carbon source. They advocated that OH radicals worked as a weak oxidizer to eradicate impurities without damaging the CNT. Zhang et al. [4] argued the effects of H radicals in the gas phase on SWCNT growth. They suggested that the balance of carbon and hydrogen radicals were vital for CNT growth. Plasma enhanced chemical vapour deposition (PECVD) has appeared as a key growth technique to yield vertically-aligned nanotubes [5]. Researchers using plasma processing have examined the correlation between a plasma gas phase and deposition mechanisms. Ostrikov et al. [6] examined $CH_4/H_2/Ar$ plasma for synthesis of carbon nanostructures. They noted that H atoms affected catalyst activity and that cations were provided as precursors for the carbon nanostructure. Denysenko et al. [7] exhibited that C_xH_y ions increased with the supply of the carbon source and that H atoms also increased with the C_xH_y molecules formed in the $CH_4/H_2/Ar$ plasma. Hydrogen plays a dual role in the PECVD growth of CNT. It acts as an activator for the dissociation of hydrocarbon species into more active species and also as an etching reagent of CNT. In the present work, we analyze the effect of hydrogen on the growth of CNTs in plasma processing, analytically. In section 2, we develop a theoretical model incorporating charging rate of the CNT, kinetics of plasma species i.e., neutral atoms, growth rate of CNT in the presence of CH_4/H_2 plasma. Results and discussions are given in section 3. Finally, the conclusion is given in section 4.

2. Model

We consider plasma comprising electrons, positively charged ions of types A and B, neutral atoms of type A and B, and CNT grown in the existence of plasma. The positively charged ions are anticipated to be singly ionized. For simplicity of the problem, average radius of MWCNT has been considered.

IOP Conf. Series: Journal of Physics: Conf. Series **836** (2017) 012017 doi:10.1088/1742-6596/836/1/012017

Charge neutrality equation

$$\frac{dZ}{d\tau} = n_{iAct} + n_{iBct} - \gamma_e n_{ect}$$

where Z=the charge on the CNT, n_{ijct}= the ion collection current for A and B type ions and n_{ct}= the number density of the CNT. Growth rate equation of the mass of CNT

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

where $m_{ct} = \frac{4}{3}\pi a^3 \rho_{ct}$is the mass of CNT and the terms are the gain in the mass density due to the collection of atomic and ionic species A. Energy balance equation for neutral atoms

$$\begin{aligned}
\frac{d}{d\tau}\left[\frac{3}{2}(n_A + n_B)k_B T_n\right] &= \left[\left(\frac{3}{2}k_B\right)(\alpha_A n_e n_{iA} + \alpha_B n_e n_{iB})(T_e + T_i)\right) + \left(\alpha_A n_e n_{iA} I_{pA} + \alpha_B n_e n_{iB} I_{pB})\right] \\
&+ \left(\frac{3}{2}k_B\right)\{n_e(v_{eA}\delta_{eA} + v_{eB}\delta_{eB})(T_e - T_n)[(v_{iAA}\delta_{iAA} + v_{iAB}\delta_{iAB})n_{iA} \\
&+ (v_{iBA}\delta_{iBA} + v_{iBB}\delta_{iBB})n_{iB}](T_i - T_n)\} + [\left(\frac{3}{2}k_B\right)n_{ct}[(1 - \gamma_{iA})n_{iAc} + n_{iBc}]T_{ct} \\
&- \left(\frac{3}{2}k_B\right)n_{ct}[n_{Ac}[\gamma_A T_n + \delta_{Act}(1 - \gamma_A)(T_n - T_{ct})] + n_{Bc}\delta_{Bct}(T_n - T_{ct})]] \\
&- \left(\frac{3}{2}k_B\right)(\beta_A n_A + \beta_B n_B)T_n - E_{diss}
\end{aligned}$$

where the first term is the power gained per unit volume by the neutral species due to the recombination of electrons and positively charged ions, the second term is the rate of power gained per unit volume by neutral atoms in elastic collisions with electrons and positively charged ions, and the third term is the energy gained per unit volume per second due to the formation of neutrals at the surface of the CNT due to accretion and elastic collisions with CNT. The fourth term refers to the thermal energy lost per unit volume per unit time by neutral atoms due to ionization. The last term is the energy dissipation rate per unit volume by neutral atoms into the surrounding atmosphere.

3. Results and discussions

We have solved the above mentioned equations along with others mentioned in the work of Sharma and Tewari [8] simultaneously for the charging of the CNT and for the kinetics and energy balance of electrons, ions, neutrals with appropriate boundary conditions, viz., at τ=0, $n_{ct}=10^6$ cm^{-3}, n_{iA0} = 0.58n_{e0}, n_{iB0}= 0.42 n_{e0}, $n_{A0} = n_{B0}$= 5.1 x 10^{11} cm^{-3}, n_{e0} = 1.1 x 10^{12} cm^{-3}, T_{e0}= 0.6 eV, T_{i0}= 2400 K, and T_{n0}= T_{ct}= 2000 K.

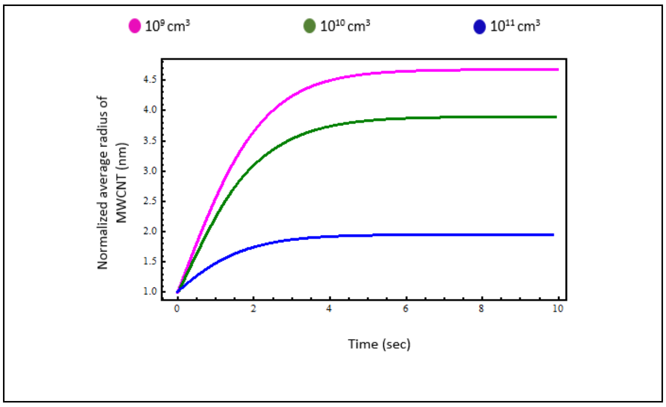

Figure 1. Time variation of normalized average radius of CNTs for different hydrogen ion density

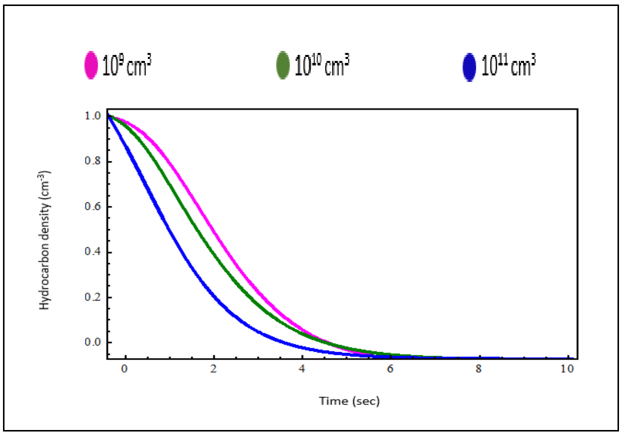

Figure 2. Time variation of hydrocarbon density of MWCNTs for different hydrogen ion density

Figure 1illustrates variation of the normalized radius of a CNT with time for different hydrogen ion number densities. It can be seen that the normalized radius of the CNT first increases with time and then attains a saturation value. The figure also shows the decrease of the normalized radius with the hydrogen ion density. This happens because for larger values of the hydrogen density, the hydrocarbon density decreases. Figure 2 illustrates variation of the hydrocarbon density with time for different hydrogen ion number densities. It can be seen that with the increase in hydrogen ion densities with time, the hydrocarbon density decreases which further affects the radius of MWCNT.

4. Conclusions

An analytical model for the growth kinetics of CNT in plasma has been developed. The approach is based on the charge neutrality and number density of electrons, positively charged ions, neutral atoms, and CNTs. It is analysed from our study that on increasing the hydrogen ion density, the hydrocarbon density and the average radius of MWCNT decreases. The above mentioned results can prove to be beneficial in the fabrication of MWCNTs.

References

[1] Iijima S 1991 *Nature* **354** 56
[2] Maruyama S, Kojima R, Miyauchi Y, Chiashi S and Kohno M 2002 *Chem. Phys. Lett.* **360** 229
[3] Hata K, Futaba DN, Mizuno K, Namai T, Yumura M and Iijima S2004 *Science* **306** 1362
[4] Zhang G, Mann D, Zhang L, Javey A, Li Y, Yenilmez E, Wang Q McVittie J P, Nishi Y, Gibbons J and Dai H 2005 *Proc. Nat. Acad. Sci. USA* **102** 16141
[5] Ostrikov K, Tzakadze Z,Rutkevych P P, Long J D, Xu S and Denysenko I 2005 *Contrib. Plasm. Phys.* **45** 7
[6] Ostrikov K 2005 *Rev. Mod. Phys.* **77** 489
[7] Denysenko I B, Xu S, Long J D, Rutkevych P P, Azarenkov N A and Ostrikov K 2004 *J. App. Phys.* **95** 2713
[8] Sharma S C and Tewari A 2011 *Phys. Plasmas* **18** 063503