Effect of Plasma Compositions on Growth and Field Emission Properties of a Spherical Carbon Nanotube (CNT) tip

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Abstract. The effect of plasma compositions (i.e., different concentration of participating ions) on growth, structure and field emission properties of spherical Carbon Nanotube (CNT) tip has been theoretically investigated. In plasma, two different kinds of positively charged ions with heavy to light ion mass ratio of 11.5 are considered and the effect of the different fractional concentrations of participating ions on the growth and field emission properties of CNT is studied. Numerical calculations of the radius of spherical CNT tip for different fractional light ion concentrations have been carried out for the typical glow discharge plasma parameters. It is found that on increasing fractional light ion concentration, the radius of spherical CNT tip decreases and consequently the field emission factor for spherical CNT tip increases.

1. Introduction
Levchenko et al. [1] have studied the growth of carbon nanocone arrays on metal catalyst and the effect of carbon flux ionization. They have found that a high degree of ionization of neutral gas in plasma leads to a better uniformity of metal catalyst saturation and nanocone growth and thereby contributes to the formation of more height – uniform arrays of carbon nanostructures. Lee et al.[2] have investigated the effect of plasma treatment on surface morphology and field emission characteristics of CNT and revealed that the plasma treatment can modify the surface morphology and enhanced the field emission characteristics of the CNTs. Srivastava et al.[3] have synthesized carbon films by microwave plasma enhanced chemical vapour deposition (MPECVD) using mixture of methane and argon gases on Ni coated and Si substrates and found that the increase in microwave power causes more ionization of the gas, which increases the density of plasma species of relatively higher energy. Moreover, increased nucleation of graphitic clusters is expected to occur and this leads to formation of carbon petals of relatively smaller size and higher density at increased microwave power.

2. Model
We consider plasma containing electrons, positively charged ions of type A and B, neutral atoms of type A and B and CNT is grown in the presence of plasma. The two ions have considerable differences
in their masses such that we consider ion \( A \) to be a light and ion \( B \) to be a heavy ion. The ratio of heavy to light ion masses is 11.5.

We have developed a model whereby changing the concentration of light positively charged ion, the corresponding change in heavy positive ion concentration is automatically obtained.

The initial radius of spherical CNT tip \( a_0 \) can be estimated by equating the accretion of electrons and light and heavy positively charged ions on the CNT, i.e.,

\[
n_e \left( \frac{T_e}{m_e} \right)^{\frac{1}{2}} \exp \left( -\frac{e^2}{a_0^2 k_B T_e} \right) = \left( 1 + \frac{e^2}{a_0^2 k_B T_i} m_{ilA} \right)^{\frac{1}{2}} + n_{ihB} \left( \frac{T_i}{m_{ihB}} \right)^{\frac{1}{2}},
\]

where \( n_e, T_e \) are the electron density and temperature, respectively. The ion temperature is denoted by \( T_i \), the Boltzmann constant by \( k_B \), and the electron charge by \( e \). The densities of light and heavy positive ions are indicated by \( n_{ilA} \) and \( n_{ihB} \) with masses \( m_{ilA} \) and \( m_{ihB} \), respectively. The plasma density, \( n_p0 \), equals the electron density, \( n_e \); consequently, with the fractional densities \( \alpha_l \) and \( \alpha_h \) of light and heavy positive ions, and\( \alpha_h = 1 - \alpha_l \), one finds \( n_{ilA} = \alpha_l n_p0 \) and \( n_{ihB} = \alpha_h n_p0 \).

### 2.1 Growth rate equation of the mass of CNT

The growth rate can be computed using

\[
\frac{dm_{ct}}{d\tau} = \left( m_{A^+} \gamma_A n_{A^+} + m_{ilA} \gamma_{ilA} n_{ilA} \right),
\]

where \( m_{ct} \) is the mass of the CNT of radius \( a \). With the density of the CNT, \( \rho_{ct} \), the mass of the CNT can be expressed in terms of the density \( m_{ct} = \frac{4}{3} \pi a^3 \rho_{ct} \). The sticking coefficients for the ionic species and the light positive ions are \( \gamma_A \) and \( \gamma_{ilA} \), respectively. The two terms in Equation (2) correspond to gain in mass due to collection of atomic and ionic species \( A \).

### 3. Results and discussion

We have carried out calculations to study the dependence of the radius of spherical CNT tip on the various compositions of ions in plasma by varying \( n_{A00} \) and \( n_{B00} \). It is the accretion of neutral atoms and positively charged ions on the CNT that leads to its growth. Different plasma compositions signify the different concentrations of participating ions. In the present analysis we have varied the concentrations of participating positively charged ions and studied its effect on radius of spherical CNT tip. The other \( \alpha \) parameters used in the calculations are the same as in Tewari et al. [4].

Figure 1 illustrates the variation of normalized radius \( a/a_0 \) of spherical CNT tip with time for different fractional concentrations of light positively charged ions, i.e., \( \alpha_l = 0.1, 0.3, 0.6 \) & 0.9. From Fig. 1 it can be seen that the normalized radius of CNT first increases with time and then attains a saturation value. It also shows the decrease of normalized radius \( a/a_0 \) with fractional concentrations of light positively charged ions, \( \alpha_l \), because for larger values more and more neutral atoms ionize to produce positively charged ions and electrons. Since it is the accretion of neutral atoms on the CNT which leads to its growth, therefore by increasing the fractional concentrations of light positively charged ions the radius of the CNT decreases.

Figure 2 shows the variation of normalized ionic density of type \( A \) in plasma with time for different values of sticking coefficients \( \gamma_A = 0.1, 0.3, 0.5 \) & 1.0. It can be seen in Fig. 2 that with increasing fractional concentrations of light positively charged ions, the positively charged ion of type \( A \) decays faster. With plasma treatment and increase in plasma power, ions of type \( A \) will decay faster leading to decrease in CNT radius which is consistent with the experimental observations of Lee et al. [2] and Srivastava et al. [3].
Figure 1. Variation of the normalized radius $a/a_0$ for spherical CNT tips for different fractional concentrations of light positive charged ions. The indicated a, b, c, d, responses correspond to $a_i = 0.1, 0.3, 0.6$ & 0.9, respectively.

Figure 2. Variation of the normalized ionic density with time for different sticking coefficients of atomic species a, b, c, d, corresponding to $\gamma_A = 0.1, 0.3, 0.5$ & 1.0, respectively.

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