Journal of Atomic, Molecular, Condensate & Nano Physics
Vol. 2, No. 3, pp. 215–227, 2015
ISSN 2349-2716 (online); 2349-6088 (print)
Published by RGN Publications

http://www.rgnpublications.com

Role of Plasma Parameters on the Growth and Field Emission Properties of 2D Graphene Sheet

Research Article

Neha Gupta, Aarti Tewari and Suresh C. Sharma*

Department of Applied Physics, Delhi Technological University, Delhi, India
***Corresponding author:** suresh321sharma@gmail.com

Abstract. The role of plasma parameters (electron density and temperature, ion density and temperature) on the growth and field emission properties of two dimensional graphene sheet has been theoretically investigated. A theoretical model of charge neutrality, including the kinetics of electrons, negatively and positively charged ions, neutral atoms and the energy balance of various species has been developed. Numerical calculations of the graphene for different plasma parameters (electron density and temperature, ion density and temperature) have been carried out for the typical glow discharge plasma parameters. It is found that the thickness of graphene sheet decreases with plasma parameters and hence the field emission of electrons from the graphene sheet increases. Some of our theoretical results are in compliance with the existing experimental observations.

Keywords. Graphene; Plasma parameters; Thickness; Field emission

PACS. 61.48.Gh

Received: February 13, 2015 **Accepted:** October 25, 2015

Copyright © 2015 Neha Gupta, Aarti Tewari and Suresh C. Sharma. *This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.*

1. Introduction

Graphene is a two-dimensional nanostructure that has a flat monolayer of carbon atoms arranged in a honeycomb crystal lattice. It is the thinnest known material in the universe and exhibits various peculiar physical properties [1].

The graphene has been synthesized by various methods like using solid-phase based method, *micro wave plasma enhanced chemical vapor deposition* (MWPECVD), exfoliation of graphite,

different solid carbon sources, using ion implantation, via propane chemical vapor deposition, self organized growth etc.

Graphene nanowalls, nanosheets and few layer graphene have been grown in the presence of plasma atmosphere on a variety of substrates without the use of catalysts [2–9] as well as in the presence of catalyst [10–15].

Yuan *et al.* [2] have reported synthesis of high-quality graphene sheets (GSs) containing 1- or 2 - 3 layers of graphene using MWPECVD in a gas mixture of methane and hydrogen. They presented that preferential etching of the inter-planar carbon bonding by hydrogen atoms in the plasma is essential for the formation of graphene structure.

Malesevic *et al.* [3] have presented a possible route for the mass production of freestanding *few layer graphene* (FLG) by means of MWPECVD. This technique is most promising since it does not rely on the use of catalyst and only require substrates material to withstand temperatures up to 700 °C.

Yu *et al.* [4] have reported a patterned synthesis of vertical graphene nanosheets using plasma-enhanced chemical vapor deposition. Their results suggest that the electric field distribution above the substrate material plays a key role in the graphene coverage.

Soin *et al.* [5] have grown vertically aligned few layered graphene (FLG) nanoflakes on Si (100) substrates by MWPECVD method. They suggested that the growth of FLGs proceeds via the nucleation of highly stressed nanocrystalline graphite layers. They also studied the time dependent growth of FLG nanoflakes.

French *et al.* [6] have prepared carbon nanosheets using radio frequency plasma-enhanced chemical vapour deposition and studied the structure of graphene sheets at different substrate temperatures. Their results suggest that the average number of graphene layers reduces significantly with increase of temperature.

Hiramatsu *et al.* [7] have fabricated *carbon nanowalls* (CNWs) on Si, SiO_2 and sapphire substrates without catalyst and have also investigated the correlation between CNW growth and fabrication conditions.

Wang *et al.* [8] have synthesized carbon nanosheets on a variety of substrates by radio-frequency plasma-enhanced chemical vapor deposition without any catalyst or special substrate treatment. They highlighted that the nanosheets consist of one to three graphene layers with a large smooth surface topography, standing roughly vertical to the substrate.

Kondo *et al.* [9] have fabricated two-dimensional carbon nanostructures, *carbon nanowalls* (CNWs), on a Si substrate using radical injection plasma-enhanced chemical vapor deposition, employing fluorocarbon (C_2F_6) and hydrogen (H_2) mixtures. They suggested that the growth rate and morphology of grown CNWs were influenced by the surface conditions of the chamber wall.

Kim *et al.* [10] have demonstrated that methane alone can provide a sufficient amount of hydrogen species for single layer synthesis on Cu foil without explicit H_2 flow by PECVD. They have observed that as the plasma power (10-15 W) increases, the grain size increases and decreases at higher plasma power (greater than 50 W), showing a saturation behavior when the plasma power is higher than 120 W.

Vizireanu *et al.* [11] have shown that high quality CNW materials can be obtained by downstream PECVD in a radio frequency plasma generated beam generated in Ar, injected with a H_2/C_2H_2 mixture. They have revealed the importance of plasma species in the growth process by investigating the correlation between the material properties and the plasma characteristics measured at different points along the flow axis.

Nandmuri *et al.* [12] have grown single and multilayer graphene films on Ni substrate by RFPECVD using remote plasma configuration.The method employed eliminates the effect of plasma electrical field on the orientation of graphene films.

Recently, Kim *et al.* [13] have reported the synthesis of single layer graphene on Cu foil in the absence of H_2 flow by PECVD. In this case, they have observed that the average grain size is $\approx 0.4\,\mu$m when the plasma power is 10 W, but it sharply increases to $\approx 3\,\mu$m when the plasma power is increased to 50 W. It also sharply decreased to $\approx 0.8\,\mu$m at a plasma power of 170 W.

Lee *et al.* [14] have reported synthesis of graphene film by DC plasma on SiO_2 substrate coated with Ni thin film. They have found that in addition to the graphene film formed at the surface of catalyst layer, a second graphene film at the catalyst/SiO_2 interface was observed.

The highly desirable properties of graphene due to its unique energy-momentum dispersion relation have attracted tremendous interest for numerous fundamental studies [15]. Owing unique properties such as high mobility, atomic thickness, excellent electrical conductivity, and high aspect ratio qualify graphene as an ideal candidate for field emission applications. The electrons in graphene behave as massless Dirac fermions and display the half-integer quantum Hall effect. The presence of large number of edges renders graphene superior to CNTs for electron tunneling. In view of above properties of graphene, extensive studies on field emission properties of graphene have been carried out.

Field emission from single layer graphene films prepared by Electrophoretic deposition has been reported by Wu *et al.* [16]. Malesevic *et al.* [17] have shown the electron field emission from pristine FLGs synthesized by MPECVD and obtained field emission with a turn-on field as low as $1\,\mathrm{V}\mu\,\mathrm{m}^{-1}$. Soin *et al.* [18] and Palnitkar *et al.* [19] explained the field emission behavior of pristine and doped FLGs. They found that N_2 plasma treated FLGs showed significant improvement in field emission characteristics. Eda *et al.* [20] reported the field emission from graphene sheets oriented at some angles with respect to the substrate surface. Zhang *et al.* [21] showed that the field enhancement factor is strongly influenced by the height, tip shape and amorphous carbon content of FLGs.

However, relations between current density and applied field, estimation of field enhancement factor [18, 22] and expression for the dependence of field enhancement factor β at the edge on the thickness, height and width [23] have also been established.

As far as author's knowledge is concerned nobody has studied the effect of plasma on the growth and field emission properties of graphene. Hence, in the present paper, we report the role of plasma on the growth and field emission properties of two dimensional graphene sheet. In Section 2, we develop a theoretical model for graphene based on the charge neutrality of graphene, including the kinetics of various species in plasma, i.e., electrons, neutral atoms, positively and negatively charged ions and number density of graphene and the energy balance of the plasma species and graphene. After that, results and discussions are presented in Section 3. Finally, the conclusion part is given in Section 4.

2. Model

Following the previous model of Sodha *et al.* [24] we consider plasma containing electrons, positively charged ions of type A and B, neutral atoms of type A and B, and graphene is grown in the presence of plasma. The positively charged ions are assumed to be singly ionized. V_s is the surface potential on the plane metallic graphene. The surface potential V_s can be estimated by equating the number of electrons striking on the graphene surface and number of ions striking on the graphene surface.

$$n_e\left(\frac{T_e}{m_e}\right)^{\frac{1}{2}}\exp\left(-\frac{eV_s}{k_BT_e}\right)=\left(1+\frac{eV_s}{k_BT_i}\right)\left[n_{iA}\left(\frac{T_i}{m_{iA}}\right)^{\frac{1}{2}}+n_{iB}\left(\frac{T_i}{m_{iB}}\right)^{\frac{1}{2}}\right]$$

or

$$\exp\left(-\frac{eV_s}{k_BT_e}\right)=\left(1+\frac{eV_s}{k_BT_i}\right)\left[\frac{n_{iA}}{n_e}\left(\frac{T_i}{T_e}\times\frac{m_e}{m_{iA}}\right)^{\frac{1}{2}}+\frac{n_{iB}}{n_e}\left(\frac{T_i}{T_e}\times\frac{m_e}{m_{iB}}\right)^{\frac{1}{2}}\right] \tag{1}$$

where

n_e = number density of electron,
T_e = electron temperature,
T_i = ion temperature,
k_B = Boltzmann's constant,
n_{iA} = number density of ion A,
m_{iA} = mass of ion A,
n_{iB} = number density of ion B,
m_{iB} = mass of ion B,
e = electronic charge,

A. Charge Neutrality Equation

$$Zn_{gn}+n_{iA}+n_{iB}=n_e, \tag{2}$$

where

Z = charge on graphene,
n_{gn} = number density of graphene.

B. Charging of the Graphene

This equation describes the charge developed on the graphene due to accretion of electrons and positively charged ions on the surface of graphene.

$$\frac{dZ}{dt}=n_{iAgn}+n_{iBgn}-\gamma_e n_{egn}, \tag{3}$$

where

$n_{egn} = A\left(\frac{2\pi k_B T_e}{m_e}\right)^{\frac{1}{2}} n_e \exp\left[-\frac{eV_s}{k_B T_e}\right]$ is the electron collection current at the graphene surface and $A = a \times b$, where a is the length and b is the height of graphene.

$n_{ijgn} = A\left(\frac{2\pi k_B T_i}{m_j}\right)^{\frac{1}{2}} n_{ij}\left\{\frac{2}{\sqrt{\pi}}\left(\frac{eV_s}{k_B T_i}\right)^{\frac{1}{2}} + \exp\left(\frac{eV_s}{k_B T_i}\right)\mathrm{erfc}\left[\left(\frac{eV_s}{k_B T_i}\right)^{\frac{1}{2}}\right]\right\}$ is the ion collection current at the graphene surface, j refers to either A or B positively charged ion and γ_e is the sticking coefficient of constituent electron at the graphene surface.

C. Growth Rate Equation of Electron Density

The equation describes the growth rate of electron density in the plasma

$$\frac{dn_e}{d\tau} = \left(\beta_A n_A + \beta_B n_B\right) - \left(\alpha_A n_e n_{iA} + \alpha_B n_e n_{iB}\right) - \gamma_e n_{gn} n_{egn}, \tag{4}$$

where β_j is the coefficient of ionization of the constituent neutral atoms due to external agency, $\alpha_j(T_e) = \alpha_{j0}\left(\frac{300}{T_e}\right)^k \mathrm{cm}^3/\mathrm{sec}$ is the coefficient of recombination of electrons and positively charged ions. The first term in Eq. (4) is the rate of gain in electron density per unit time on account of ionization of neutral atoms and second term is the decaying rate of the electron density due to electron-ion recombination and the third term is the electron collection current at the surface of graphene.

D. Growth Rate Equation of Positively Charged Ion Density

The equation describes the growth rate equation of positively charged ions in plasma

$$\frac{dn_{iA}}{d\tau} = \beta_A n_A - \alpha_A n_e n_{iA} - n_{gn} n_{iAgn}, \tag{5}$$

$$\frac{dn_{iB}}{d\tau} = \beta_B n_B - \alpha_B n_e n_{iB} - n_{gn} n_{iBgn}. \tag{6}$$

The first term in Eqs. (5) and (6) is the gain in ion density per unit time on account of ionization of neutral atoms, second term is the electron-ion recombination and third term is the ion collection current to the surface of graphene.

E. Growth Rate Equation of Neutral Atoms

The equation describes the growth rate equation of neutral atoms in plasma

$$\frac{dn_A}{d\tau} = \alpha_A n_e n_{iA} - \beta_A n_A + n_{gn}\left(1 - \gamma_{iA}\right) n_{iAgn} - n_{gn}\gamma_A n_{Agn}, \tag{7}$$

$$\frac{dn_B}{d\tau} = \alpha_B n_e n_{iB} - \beta_B n_B + n_{gn} n_{iBgn}, \tag{8}$$

where $n_{jgn} = A\left(\frac{2\pi k_B T_n}{m_j}\right)^{\frac{1}{2}} n_j$ is the neutral collection current at the surface of graphene. The first term in Eqs. (7) and (8) is the gain in neutral atom density per unit time due to electron-ion recombination, second term is the decrease in neutral density due to ionization, third term is the gain in neutral density due to neutralization of the atoms collected at the surface of graphene and the last term in Eq. (7) is the accretion of neutral atoms of species A on the surface of graphene.

F. Growth Rate Equation of the Mass of Graphene

$$A\rho_s \frac{dz}{d\tau} = m_A \gamma_A n_{Agn} + m_{iA}\gamma_{iA} n_{iAgn}, \tag{9}$$

where $A = (a \times b)$ is area of two dimensional graphene, ρ_s is the surface mass density of graphene and z is the thickness of graphene. The terms are the gain in mass density due to collection of atomic and ionic species A.

G. Energy Balance Equation of the Electrons

$$\begin{aligned}\frac{d}{d\tau}\left(\frac{3}{2}n_e k_B T_e\right) = {} & \left(\beta_A n_A \varepsilon_A + \beta_B n_B \varepsilon_B\right) - \left(\frac{3}{2}k_B\right)(\alpha_A n_e n_{Ai} + \alpha_B n_e n_{Bi})T_e \\ & - n_{gn} n_{egn}\left\{\gamma_e \varepsilon^{lh}_{egn} + \delta_{egn}\left(1-\gamma_e\right)\left[\varepsilon^{s}_{egn} - \left(\frac{3}{2}k_B\right)T_{gn}\right]\right\} \\ & - \left(\frac{3}{2}k_B\right)[f_{eA}\delta_{eA} + f_{eB}\delta_{eB}](T_e - T_n)n_e \\ & - \left(\frac{3}{2}k_B\right)(f_{eAi}\delta_{eAi} + f_{eBi}\delta_{eBi})(T_e - T_i)n_e,\end{aligned} \tag{10}$$

where T_n is the temperature of neutral atoms, T_{gn} is the temperature of graphene, ε_j is the mean energy of electrons due to ionization of neutral atoms, $\varepsilon^{lh}_{egn}(Z) = \varepsilon^{s}_{egn}(Z) - eV_s$ is the mean energy of electrons (at large distance from the surface of graphene) collected by graphene, $\varepsilon^{s}_{egn}(Z) = 2k_B T_e$ is the mean energy of electrons collected by graphene, $f_{ej} = f_{ej0}\left(\frac{n_j}{n_{j0}}\right)\left(\frac{T_e}{T_{e0}}\right)^{\frac{1}{2}}$ is the electron collision frequency due to elastic collisions with neutral atom, and $f_{ej0} = (8.3\times10^5)$ $\pi {r_j}^2 n_{j0} {T_{e0}}^{\frac{1}{2}}$, $f_{eji} = f_{eji0}\left(\frac{n_{ji}}{n_{ji0}}\right)\left(\frac{T_e}{T_{e0}}\right)^{-\frac{3}{2}}$ is the electron collision frequency due to elastic collisions with positively charged ions, and $f_{eji0} = \left(5.5\frac{n_{i0}}{T_{e0}^{\frac{3}{2}}}\right)\ln\left(\frac{220T_{e0}}{n_{i0}^{\frac{1}{3}}}\right)$, $\delta_{ej}\left[\approx 2\frac{m_e}{m_j}\right]$ is the fraction of excess energy of electron lost in a collision with the neutral atom, $\delta_{eji}\left[\approx 2\frac{m_e}{m_{ji}}\right]$ is the fraction of excess energy of electron lost in a collision with positively charged ion, $\delta_{egn}\left[\approx 2\frac{m_e}{m_{gn}}\right]$ is the fraction of excess energy of electron lost in a collision with graphene, m_j is the mass of neutral atom, r_j is the mean radii of atomic and ionic species, n_j is the number density of neutral atoms, T_{e0} is the temperature of electrons in the absence of graphene, $\frac{f_{ej0}}{f_{eij0}}$ is the electron collision frequency due to collisions with atoms/ions in the absence of graphene, n_{e0} is the initial number density of electrons, and n_{j0} is the initial number density of neutral atom.

The first term on the right hand side in Eq. (10) is the power gained per unit volume by electrons due to ionization of neutral atoms, second term is the energy loss per unit volume per unit time due to recombination with positively charged ions in plasma, third term is the energy loss per unit volume per unit time due to the sticking accretion and elastic collisions of electrons at the surface of graphene, fourth term is the energy loss per unit volume per unit time due to elastic electron - atom collision and fifth term is the energy loss per unit volume per unit time due to elastic electron- ion collision .

Substituting the value of $\frac{dn_e}{d\tau}$ from Eq. (4) in Eq. (10), we get

$$\begin{aligned}\left(\frac{3}{2}k_B\right)n_e\left(\frac{dT_e}{d\tau}\right) = &\left[\left(\beta_A n_A \varepsilon_A + \beta_B n_B \varepsilon_B\right) - \left(\frac{3}{2}k_B\right)\left(\beta_A n_A + \beta_B n_B\right)T_e\right] \\ &- n_{gn}n_{egn}\left\{\gamma_e\left[\varepsilon^l_{egn} - \left(\frac{3}{2}k_B\right)T_e\right]\right. \\ &\left.+\delta_{egn}\left(1-\gamma_e\right)\left[\varepsilon^s_{egn} - \left(\frac{3}{2}k_B\right)T_{gn}\right]\right\} - \left(\frac{3}{2}k_B\right) \\ &\times\left[f_{eA}\delta_{eA} + f_{eB}\delta_{eB}\right](T_e - T_n)n_e - \left(\frac{3}{2}k_B\right) \\ &\times\left[f_{eAi}\delta_{eAi} + f_{eBi}\delta_{eBi}\right](T_e - T_i)n_e. \end{aligned} \tag{11}$$

H. Energy Balance Equation for Positively Charged Ions

$$\begin{aligned}\frac{d}{d\tau}\left[\frac{3}{2}(n_{iA}+n_{iB})k_B T_i\right] = &\left(\beta_A n_A \varepsilon_{iA} + \beta_B n_B \varepsilon_{iB}\right) + \left(\frac{3}{2}k_B\right) \\ &\times n_e\left[f_{eAi}\delta_{eAi} + f_{eBi}\delta_{eBi}\right](T_e - T_i) \\ &- \left(\frac{3}{2}k_B\right)(\alpha_A n_e n_{iA} + \alpha_B n_e n_{iB})T_i \\ &- n_{gn}\left[n_{iAgn}\varepsilon^l_{iAgn} + n_{iBgn}\varepsilon^l_{iBgn}\right] - \left(\frac{3}{2}k_B\right) \\ &\times\left[\left(f_{iAA}\delta_{iAA} + f_{iAB}\delta_{iAB}\right)n_{iA}\right. \\ &\left.+\left(f_{iBA}\delta_{iBA} + f_{iBB}\delta_{iBB}\right)n_{iB}\right](T_i - T_n), \end{aligned} \tag{12}$$

where $\varepsilon^l_{ijgn}(Z) = \left(2 - \frac{eV_s}{k_B T_i}\right)k_B T_i$ is the mean energy of positively charged ions (at large distance from the surface of graphene) collected by graphene, ε_{ij} is the mean energy of positively charged ions produced by the ionization of neutral atoms, $f_{ijj'} = f_{ijj'0}\left(\frac{n_{j'}}{n_{j'0}}\right)\left(\frac{m_{j'}T_i + m_{ij}T_n}{(m_{j'}T_{i0} + m_{ij}T_{n0})}\right)^{\frac{1}{2}}$ is the collision frequency of a j type of ion with j' ion of neutral atom, $\delta_{ijj'} = \left[\frac{2m_{ij}}{(m_{j'}+m_{ij})}\right]$ is the fraction of excess energy of a j type positively charged ion, lost in a collision with neutral j' kind of neutral atom, $f_{ijj'0} = \left(\frac{8}{3}\right)(2\pi k_B)^{\frac{1}{2}}(r_{ij} + r_{j'})^2\left(\frac{n_{j'0}m_{j'}}{(m_{ij}+m_{j'})}\right)\left[\left(\frac{T_{i0}}{m_{ij}}\right) + \left(\frac{T_{n0}}{m_{j'}}\right)\right]^{\frac{1}{2}}$, T_{i0} and T_{n0} are the initial temperatures of positively charged ions and neutrals, respectively

The first term on the right hand side in Eq. (12) is the energy gained per unit volume per unit time by the positively charged ions due to ionization of atoms, second term refers to the energy gained per unit volume per unit time due to elastic collision of ions with electrons, third term is the energy loss per unit volume per unit time due to electron-ion recombination, fourth term is the energy loss per unit volume per unit time due to sticking accretion of ions at the surface of graphene and last term is the energy lost per unit volume per unit time on account of elastic collision with neutral species. Since both species of ions are assumed to be at the same temperature, the ion-ion collisions do not contribute to the energy balance.

Substituting the value of $\frac{dn_i}{d\tau}$ from Eq. (5) and Eq. (6) in Eq. (12), we get

$$\left(\frac{3}{2}k_B\right)(n_{iA}+n_{iB})\left(\frac{dT_i}{d\tau}\right)=\left[\left(\beta_A n_A\varepsilon_{iA}+\beta_B n_B\varepsilon_{iB}\right)-\left(\frac{3}{2}k_B\right)\left(\beta_A n_A+\beta_B n_B\right)T_i\right]$$
$$+\left(\frac{3}{2}k_B\right)n_e[f_{eAi}\delta_{eAi}+f_{eBi}\delta_{eBi}](T_e-T_i)$$
$$-n_{gn}\left[n_{iAgn}\left[\varepsilon^l_{iAgn}-\left(\frac{3}{2}k_B\right)T_i\right]+n_{iBgn}\left[\varepsilon^l_{iBgn}-\left(\frac{3}{2}k_B\right)T_i\right]\right]$$
$$-\left(\frac{3}{2}k_B\right)[(f_{iAA}\delta_{iAA}+f_{iAB}\delta_{iAB})n_{iA}$$
$$+(f_{iBA}\delta_{iBA}+f_{iBB}\delta_{iBB})n_{iB}](T_i-T_n). \tag{13}$$

I. Energy Balance Equation for Neutral Atoms

$$\frac{d}{d\tau}\left[\frac{3}{2}(n_A+n_B)k_BT_n\right]=\left[\left(\frac{3}{2}k_B\right)(\alpha_A n_e n_{iA}+\alpha_B n_e n_{iB})(T_e+T_i)\right]$$
$$+\left(\alpha_A n_e n_{iA}I_{pA}+\alpha_B n_e n_{iB}I_{pB}\right)+\left(\frac{3}{2}k_B\right)[n_e(f_{eA}\delta_{eA}$$
$$+f_{eB}\delta_{eB})(T_e-T_n)+[(f_{iAA}\delta_{iAA}+f_{iAB}\delta_{iAB})n_{iA}$$
$$+(f_{iBA}\delta_{iBA}+f_{iBB}\delta_{iBB})n_{iB}](T_i-T_n)]$$
$$+\left(\frac{3}{2}k_B\right)n_{gn}\left[(1-\gamma_{iA})n_{iAgn}+n_{iBgn}\right]T_{gn}$$
$$-\left(\frac{3}{2}k_B\right)n_{gn}\left[n_{Agn}\left[\gamma_A T_n+\delta_{Agn}(1-\gamma_A)(T_n-T_{gn})\right]\right.$$
$$\left.+n_{Bgn}\delta_{Bgn}(T_n-T_{gn})\right]$$
$$-\left(\frac{3}{2}k_B\right)(\beta_A n_A+\beta_B n_B)T_n-E_{diss}, \tag{14}$$

where

I_{pj} is the ionization energy of the constituent atomic species,

$E_{diss}=\left(E_{A,diss}+E_{B,diss}\right)$, $E_{j,diss}$ is the energy dissipated per unit volume per unit time by neutral atoms to the surrounding atmosphere, $\delta_{jgn}=\left[\frac{2m_j}{(m_j+m_{gn})}\right]$ is the fraction of excess energy of an atom lost in a collision with the graphene, T_a is the ambient temperature. The dissipation energy may be assumed to be proportional to the difference between the temperatures of the neutral atomic species T_n and the ambient temperature T_a.

$E_{j,diss}=E_{j,diss0}\left[\frac{(T_j-T_a)}{(T_{j0}-T_a)}\right]$.

The constant $E_{j,diss0}$ is easily obtained by imposing the ambient condition of the complex plasma system in Eq. (14) for both constituent neutral species.

The first term on the right hand side of Eq. (14) is the power gained per unit volume by the neutral species due to recombination of electron and positively charged ions, second term is

the rate of power gained per unit volume by neutral atoms in elastic collision with electrons and positively charged ions, respectively, third term is the energy gained per unit volume per second due to formation of neutrals at the surface of the graphene on account of electron and ion collection currents. The fourth term refers to the power loss per unit volume due to sticking accretion and elastic collisions with graphene. The next 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 to the surroundings

Substituting the value of $\frac{dn_A+n_B}{d\tau}$ from Eq. (7) and Eq. (8) in Eq. (14), we get

$$\begin{aligned}\frac{3}{2}(n_A+n_B)k_B\left(\frac{dT_n}{d\tau}\right) = &\left[\left(\frac{3}{2}k_B\right)(\alpha_A n_e n_{iA}+\alpha_B n_e n_{iB})(T_e+T_i-T_n)\right]\\ &+\left(\alpha_A n_e n_{iA} I_{pA}+\alpha_B n_e n_{iB} I_{pB}\right)\\ &+\left(\frac{3}{2}k_B\right)[(f_{iAA}\delta_{iAA}+f_{iAB}\delta_{iAB})n_{iA}\\ &+(f_{iBA}\delta_{iBA}+f_{iBB}\delta_{iBB})n_{iB}](T_i-T_n)\\ &+\left(\frac{3}{2}k_B\right)n_e(f_{eA}\delta_{eA}+f_{eB}\delta_{eB})(T_e-T_n)\\ &+\left(\frac{3}{2}k_B\right)n_{gn}[(1-\gamma_{iA})n_{iAgn}+n_{iBgn}](T_{gn}-T_n)\\ &-\left(\frac{3}{2}k_B\right)n_{gn}[n_{Agn}\delta_{gn}(1-\gamma_A)(T_n-T_{gn})\\ &+n_{Bgn}\delta_{Bgn}(T_n-T_{gn})]-E_{diss}. \end{aligned} \tag{15}$$

J. Energy Balance for Metallic Graphene

$$\begin{aligned}\frac{d}{d\tau}\left(A\rho_s z C_p T_{gn}\right) = &\, n_{egn}\left[\gamma_e\varepsilon^s_{egn}+\left(1-\gamma_e\right)\delta_{egn}\left[\varepsilon^s_{egn}-\left(\frac{3}{2}k_B\right)T_{gn}\right]\right]+n_{Bgn}\delta_{Bgn}(T_n-T_{gn})]\\ &\times[n_{iAgn}(\varepsilon^s_{iAgn}+I_{pA})+n_{iBgn}(\varepsilon^s_{iBgn}+I_{pB})]\\ &-\left(\frac{3}{2}k_B\right)\left[n_{Agn}\left[\gamma_A T_n+\delta_{Agn}\left(1-\gamma_A\right)\left(T_n-T_{gn}\right)\right]\right.\\ &-\left(\frac{3}{2}k_B\right)\left[\left(1-\gamma_{Ai}\right)n_{iAgn}+n_{iBgn}\right]T_{gn}-A\left[\varepsilon\sigma\left({T_{gn}}^4-{T_a}^4\right)\right.\\ &+\left[n_A\left(\frac{8k_BT_n}{\pi m_A}\right)^{\frac{1}{2}}+n_B\left(\frac{8k_BT_n}{\pi m_B}\right)^{\frac{1}{2}}\right]k_B\left(T_{gn}-T_n\right)], \end{aligned} \tag{16}$$

where $\varepsilon^s_{ijgn}(Z)=\left(\left(\frac{\left(2-\frac{eV_s}{k_BT_i}\right)}{\left(1-\frac{eV_s}{k_BT_i}\right)}\right)-\frac{eV_s}{k_BT_i}\right)k_BT_i$ is the mean energy collected by ions at the surface of graphene, C_p is the specific heat of the material of the graphene at constant pressure, ε is the emissivity of the material of the graphene, σ is the Stefan-Boltzmann constant.

The first three terms in Eq. (16) are the rate of energy transferred to the graphene due to sticking accretion and elastic collision by constituent species of complex plasma. The fourth

term is the energy carried away by the neutral species (generated by the recombination of the accreted ions and electrons) from the graphene per unit volume per unit time. The last term is the rate of energy dissipation of the graphene through radiation and conduction to the host gas.

3. Results and Discussions

The calculations have been carried out to study the dependence of thickness of graphene on the plasma parameters, i.e., n_e, T_e, n_i, T_i.

We have solved the Eqs. (2), (3), (4), (5), (6), (7), (8), (9), (13), (15) and (16) simultaneously for charging of graphene, kinetics and energy balance of electrons, ions, neutrals and of graphene with appropriate boundary conditions, viz., at $\tau = 0$, graphene number density $(n_{gn}) = 10^4$ cm^{-3}, ion number density of type A $(n_{iA0} = 0.8n_{e0})$, ion number density of type B $(n_{iB0} = 0.2n_{e0})$, neutral atom number density of type A and B $(n_{A0}$ and $n_{B0}) = (1 \times 10^{10}$ cm$^{-3})$, electron number density $(n_{e0}) = (10^8$ cm$^{-3})$, electron temperature $T_{e0} = 0.8$ eV, ion temperature $T_{i0} = 2400$ K, neutral temperature T_{n0} = graphene temperature $T_{gn} = 2000$ K, a (length of graphene) = 5 μm, b (height of graphene) = 5 nm.

Other parameters used in the calculations are, e.g., mass of ion A $(m_{iA}) \approx$ mass of neutral atom A $(m_A) = 12$ amu (Carbon), mass of ion B $(m_{iB}) \approx$ mass of neutral atom B $(m_B) = 39.948$ amu (Argon), coefficient of recombination of electrons and positive ion of type A and B $(\alpha_{A0} \approx \alpha_{B0}) = 10^{-7}$ cm^3/sec, emissivity of material of graphene $(\varepsilon) = 0.6$, sticking coefficient of ion A and neutral atom A $(\gamma_A = \gamma_{iA}) = 1$, work function of graphene $\phi = 5$ eV (Carbon), specific heat of graphene $C_p = 7 \times 10^6$ ergs/gK, ionization energy of neutral atom A $(I_{pA}) = 5.26$ eV, ionization energy of neutral atom B $(I_{pB}) = 7$ eV, $\varepsilon_A = 4.69$ eV, $\varepsilon_B = 6.7$ eV, mean energy of positively charged ions produced by the ionization of neutral atom A $(\varepsilon_{iA}) = 4.78$ eV, mean energy of positively charged ions produced by the ionization of neutral atom B $(\varepsilon_{iB}) = 7.03$ eV, dissipation energy of neutral atom A $(\varepsilon_{A,diss0}) = 1820.9$ eV, dissipation energy of neutral atom B $(\varepsilon_{B,diss0}) = 799.6$ eV, $\kappa = -1.2$, initial thickness $z_0 = 4$ nm and density of graphene $\rho_{gn} = 2.2$ g/cm^3, surface potential $V_s = -400$ stat V.

Figure 1 illustrates the variation of normalized thickness of graphene sheet for different electron density and temperature (e.g., $n_{e0} = 10^7$ cm^{-3} and $T_{e0} = 0.6$ eV, $n_{e0} = 10^8$ cm^{-3} and $= T_{e0} = 0.7$ eV, $n_{e0} = 10^9$ cm^{-3} and $T_{e0} = 0.8$ eV) and for other parameters are same as mentioned above. From Figure 1 it can be seen that the normalized thickness of graphene first increases with time and then attains a saturation value. It also shows the decrease of normalized thickness of graphene z/z_0 with electron density and temperature. The decrease of z/z_0 with electron density and temperatures is because with increase in electron densities and temperatures more and more neutral atoms ionizes to produce positively charged ions and electrons. Since, on the increase of electron density and temperature, the surface potential on graphene surface increases which corresponds to lesser number of ions and neutral atoms sticking to graphene surface, the decrease in its thickness is observed.

Figure 2 displays the variation of the normalized thickness of graphene z/z_0 with time for different ion number density and ion temperatures (e.g., $n_{i0} = 10^8$ cm^{-3} and $T_{i0} = 2100$ K, $n_{i0} = 10^9$ cm^{-3} and $T_{i0} = 2200$ K, $n_{i0} = 10^{10}$ cm^{-3} and $T_{i0} = 2300$ K). From Figure 2 it can be seen that the thickness of graphene first increases with time and then attains a saturation

value. The thickness of graphene decreases with ion density n_{i0} (in cm^{-3}) and temperature T_i (in K) can also be seen. This happens because by increasing the ion density and temperatures, more and more neutral atoms ionize to produce positively charged ions and electrons. The reason behind the decrease in thickness of graphene with ion density and temperature is the increase of surface potential on graphene surface as explained for Figure 1.

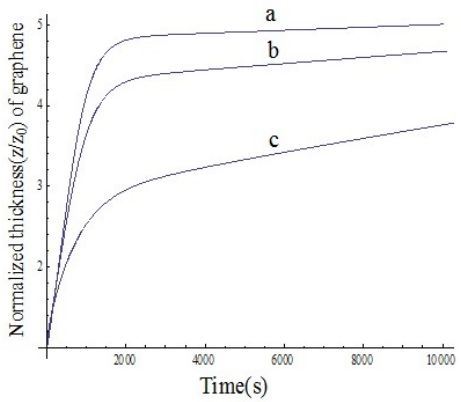

Figure 1. Shows the variation of the normalized thickness z/z_0 of graphene sheet for different electron number density and temperature where a, b and c corresponds to $n_{e0} = 10^7$ cm^{-3} and $T_{e0} = 0.6$ eV, $n_{e0} = 10^8$ cm^{-3} and $= T_{e0} = 0.7$ eV, $n_{e0} = 10^9$ cm^{-3} and $T_{e0} = 0.8$ eV, respectively (the other parameters are given in the text).

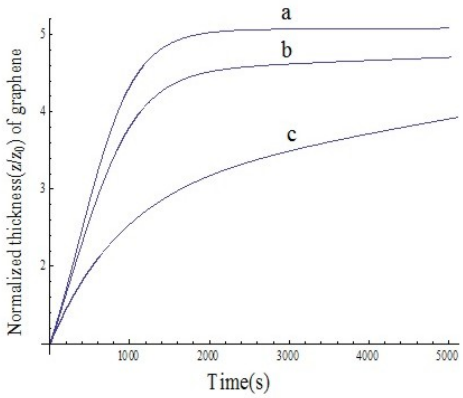

Figure 2. Shows the variation of the normalized thickness z/z_0 of graphene sheet for different ion number density and temperature where a, b and c corresponds to $n_{i0} = 10^8$ cm^{-3} and $T_{i0} = 2100$ K, $n_{i0} = 10^9$ cm^{-3} and $T_{i0} = 2200$ K, $n_{i0} = 10^{10}$ cm^{-3} and $T_{i0} = 2300$ K, respectively (the other parameters are given in the text).

The variation of graphene's thickness in plasma has also been experimentally demonstrated by French *et al.* [6] where there is reduction in graphene's thickness with increasing substrate temperature. Our results are also consistent with Nang and Kim [28] and Kim *et al.* [13] where they have shown that graphene thickness decreases with increasing plasma power and growth time because of the etching by atomic H. Moreover, with increase in electron density and temperatures (plasma parameters), ions of A type will decay faster leading to decrease in dimensions of nanostructures which is consistent with the experimental observations of Lee *et al.* [25] and Srivastava *et al.* [26].

Using the results obtained, the variation of the field emission factor with plasma parameters can be estimated. Since the field emission factor [23]

$$\beta_{edge} = 1.77\left(\frac{h}{t}\right)^{0.75}\left[1+0.09\left(\frac{h}{w}\right)\right][0.75+0.25\cos\phi]\left(\frac{d}{t}\right)^{-0.19},$$

where h is the height of graphene and t is the thickness of graphene) is inversely proportional to the thickness of graphene. From the above discussions, it is clear that the thickness of graphene decreases with increase of the plasma parameters (i.e., plasma density and temperatures) therefore, the increase in plasma parameters should lead to larger β_{edge}. The increase in field enhancement factor β, is proportional to the increase in the field emission current [18–22], so from our results it is clear that through varying plasma parameters, we can obtain larger β or field emission current. The above observation have also been validated by Peltekis *et al.* [27] where graphene ribbons have electron and hole field-effect mobilities of 11.2 and 31.9 cm^2/V_s, respectively prior to treatment and 44.8 and 143.6 cm^2/V_s, respectively after treatment. The increased mobilities of electron and hole from plasma treated graphene imply increased current from graphene.

4. Conclusion

An analytical model for the growth kinetics of the graphene in complex plasma has been developed. The approach is based on the charge neutrality, number density of electrons, positively charged ions, neutral atoms and graphene. The energy balance of the participating species has also been considered because the accretion process gets significantly affected by the increase of electron and ion temperatures. It can be concluded from our study that on increasing the plasma parameters, the thickness of graphene sheet reduces and consequently the field emission factor increases. The present analysis presents the growth mechanism involved in growing graphene in plasma which has been widely reported and extending recent studies to correlate graphene's thickness in plasma with plasma parameters and estimating the field enhancement factor of graphene.

Acknowledgement

This work has been partially supported by the Department of Science and Technology (DST), SERB, Government of India.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos and A.A. Firsov, *Nature* **438**, 197 (2005).

[2] G.D. Yuan, W.J. Zhang, Y. Yang, Y.B. Tang, Y.Q. Li, J.X. Wang, X.M. Meng, Z.B. He, C.M.L. Wu, I. Bello, C.S. Lee and S.T. Lee, *Chem. Phys. Lett.* **467**, 361 (2009).

[3] A. Malesevic, R Vitchev, K. Schouteden, A. Volodin, L. Zhang, G. Van Tendeloo, A. Vanhulsel and C.V. Haesendonck, *Nanotechnology* **19**, 305604 (2008).

[4] K. Yu, P. Wang, G. Lu, K.H. Chen and Z. Bo, *J. Chen. Phys. Chem. Lett.* **2**, 537 (2011).

[5] N. Soin, S.S. Roy, C. O'Kane, J.A.D. McLaughlin, T.H. Lim and C.J.D. Hetherington, *Cryst. Eng. Comm.* **13**, 312 (2011).

[6] B.L. French, J.J. Wang, M.Y. Zhu and B.C. Holloway, *J. Appl. Phys.* **97**, 114317 (2005).

[7] M. Hiramatsu, K. Shiji, H. Amano and M. Hori, *Appl. Phys. Lett.* **84**, 4708 (2004).

[8] J.J. Wang, M.Y. Zhu, R.A. Outlaw, X. Zhao, D.M. Manos, B.B. Holloway and V.P. Mammana, *Appl. Phys. Lett.* **85**, 1265 (2004).

[9] S. Kondo, M. Hori, K. Yamakawa, Shoji den, H. Kano and M. Hiramatsu, *J. Vac. Sci. Technol. B* **26**, 4 (2008).

[10] Y.S. Kim, J.H. Lee, Y.D. Kim, S.-K. Jerng, K. Joo, E. Kim, J. Jung, E. Yoon, Y.D. Park, S. Seo and S.-H. Chun, *Nanoscale* **5**, 1221 (2013).

[11] S. Vizireanu, S.D. Stoica, C. Luculescu, L.C. Nistor, B. Mitu and G. Dinescu, *Plasma Sources Sci. Technol.* **19**, 034016 (2010).

[12] G. Nandamuri, S. Roumimov and R. Solanki, *Appl. Phys. Lett.* **96**, 154101 (2010).

[13] K.Y. Seung, L.J. Hong, K.Y. Duck, J. Sahng-Kyoon, K. Joo, E. Kim, J. Jung, E. Yoon, P.Y. Daniel, S. Sunae and C. Seung-Hyun, *Nanoscale* **5**, 1221 (2013).

[14] C.S. Lee, L. Barton, Z.B. He, J.L. Maurice, D. Pribat and D. Cojocaru, *Phys. Rev.* **82**, 153412 (2010).

[15] A.K. Geim and K.S. Novoselov, *Nat. Mater.* **6**, 18 (2007).

[16] Z. Shuai, S. Pei, W. Ren, D. Tang, L. Gao, B. Liu, F. Li, C. Liu and H.M. Cheng, *Adv. Mater.* **21**, 1756 (2009).

[17] A. Malesevic, R. Kemps, A. Vanhulsel, M.P. Chowdhury, A. Volodin and C.V. Haesendonck, *J. Appl. Phys.* **104**, 084301 (2008).

[18] N. Soin, S.S. Roy, S. Roy, K.S. Hazra, D.S. Misra, T.H. Lim, C.J. Hetherington and J.A. McLaughlin, *J. Phys. Chem. C* **115**, 5366 (2011).

[19] U.A. Palnitkar, R.V. Kashid, M.A. More, D.S. Joag, L.S. Panchakarla and C.N.R. Rao, *Appl. Phys. Lett.* **97**, 063102 (2010).

[20] G. Eda, H.E. Unalan, N. Rupesinghe, G.A.J. Amaratunga and M. Chhowalla, *Appl. Phys. Lett.* **93**, 233502 (2008).

[21] Y. Zhang, J. Du, S. Tang, P. Liu, S. Deng, J. Chen and N. Xu, *Nanotechnology* **23**, 015202 (2012).

[22] T.T. Baby and S. Ramprahbu, *J. Appl. Phys.* **111**, 04311 (2012).

[23] S. Watcharotone, R.S. Ruoffa and F.H. Read, *Physics Procedia* **1**, 71 (2008).

[24] M.S. Sodha, S. Misra, S.K. Mishra and S. Srivastava, *J. Appl. Phys.* **107**, 103307 (2010).

[25] S.F. Lee, Y.-P. Chang and L.-Y. Lee, *J. Mater. Sci. Mater. Electron* **20**, 851 (2009).

[26] S.K. Srivastava, A.K. Shukla, V.D. Vankar and V. Kumar, *Thin Solid Films* **515**, 1851 (2006).

[27] N. Peltekias, S. Kumar, N. McEvoy, K. Lee, A. Weidlich and G. S. Duesberg, *Carbon* **50**, 395 (2012).

[28] L.V. Nang and E.T. Kim, *Journal of The Electrochemical Society* **159**, K-93 (2012).