Theoretical investigation on the effect of nitrogen doping on the growth and field emission properties of the plasma-grown graphene sheet

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Abstract. A theoretical model to study the impact of nitrogen-doping on the plasma-assisted growth and field emission properties of the graphene sheet (GS) has been developed. The model incorporates the charging rate of the GS, kinetics and energy balance of all plasma species i.e., electrons, positively charged ions and neutral atoms along with the nitrogen doping species, and growth rate of the GS. Numerical calculations on the effect of nitrogen doping on the thickness of the GS have been carried out for typical glow discharge parameters. It is found that the thickness of the GS decreases with nitrogen doping. The ramifications of nitrogen doping on the field enhancement factor of GS have likewise been examined on the premise of the above result. It is observed that the nitrogen doped GS exhibits better field emission as compared to undoped GS. Some of the results of the present investigation are in compliance with the experimental observations.

1. Introduction
Doping of graphene sheet (GS) using plasma enhanced chemical vapor deposition (PECVD) is considered as an effective method to deterministically control the growth of GS at low temperatures [1]. Mehdipour et al.[2] and Sharma et al.[3] have developed the theoretical model to study the growth of carbon nano fibers and GS in the plasma environment respectively. Nitrogen is considered as one of the most popular candidate for doping of GS as it has similar radii as that of carbon and thus can replace carbon atoms in the graphene to induce n-type conduction in graphene [4]. Seo et al.[1] have reported that the thickness of the GS reduces upon addition of nitrogen to the CH₄/Ar/H₂ gas mixture. Moreover, the nitrogen doped GS exhibits high field enhancement factor [5] (β ≈ (λ₉gr/τ₉gr), where λgs is the height and τgs is the thickness of the GS) in comparison to undoped GS [6, 7].

2. Model
Following Sodha et al. [8], the present model considers the embryonic growth of GS in complex plasma consisting of electrons, positively charged ions and neutrals of CH₄ (denoted as A), neon (denoted as B), and nitrogen (denoted as C). Here, nitrogen is considered as the doping material. The growth of GS in plasma environment can occur by many ways, namely, cluster formation, nucleation, coagulation, and growth of embryonic GS by condensation [9]. However, in the present investigation, we consider the embryonic growth of GS by condensation as we aim to explore the effect of nitrogen doping on the growth and field emission properties of the GS. Since the field
enhancement factor $\beta$ of carbon nanostructures is less influenced by the height of the carbon nanostructures [10], we study the influence of nitrogen doping on the thickness of the GS.

2.1. Growth rate equation of the mass of graphene sheet

$$\alpha_{gr} \rho_{gr} \frac{d\tau_{gr}}{dt} = \sum_k M_k \chi_k I_{kgr} + \sum_k M_{ik} \chi_{ik} I_{ikgr},$$

(1)

where $\alpha_{gr}$ ($=l_{gr} \times \lambda_{gr}$) is the area, $l_{gr}$ is the length of the GS, and $\rho_{gr}$ is the surface mass density of the GS. $M_k$ and $M_{ik}$ are the masses of atom and ion $k$ ($k$ refers to A and C type of atom or ion), respectively. Equation (1) describes the increase in thickness of the GS due to atomic ($I_{kgr}$) and ion collection current ($I_{ikgr}$) of species A and C. $\chi_k$ and $\chi_{ik}$ are the sticking coefficients of atom and ion of type $k$, respectively.

2.2. Kinetic equation of positively charged ions and neutral atoms

$$\frac{dn_k}{dt} = \varepsilon_k n_k - \delta_k n_k \eta_k - \eta_{gr} I_{gr},$$

(2)

$$\frac{dn_k}{dt} = \delta_k n_k \eta_k - \varepsilon_k n_k - \eta_k (1 - \chi_k) I_{kgr} - \eta_{gr} \chi_k I_{gr},$$

(3)

where $n_k$ and $\eta_k$ are the number densities of atom and ion of type $k$ ($k$ refers to A, B or C type of atom or ion), respectively.

Equation (2) represents the kinetics of positively charged ions, (here, $k$ refers to A, B or C type of ion) in the plasma due to ionization of neutral atoms ($\varepsilon_k$ is the coefficient of ionization), recombination of electrons and ions ($\delta_k$ is the coefficient of recombination), and ion collection current at the GS surface.

Equation (3) describes the kinetics of neutral atoms in the plasma due to electron-ion recombination, ionization of neutral atoms, ion collection current at the GS surface, and the accretion of neutral atoms A and C at the surface of GS. However, the last term of equation 3 i.e., the accretion of neutral atoms would not be accounted for the kinetics of neutral atom B.

3. Results and discussions

We have carried out the calculations to study the effect of nitrogen doping on the growth and field emission properties of the GS for typically glow discharge parameters. In particular, we have estimated the time variation of thickness of GS for undoped and nitrogen doped GS, and then premeditated the repercussion of nitrogen doping on the field enhancement factor $\beta$ of the GS. The figure 1 illustrates the variation of thickness of undoped and nitrogen doped GS with time. It can be seen from figure 1 that the thickness of GS decreases upon nitrogen doping. This can be attributed to the fact that the nitrogen atom, being pentavalent produces an extra electron on the GS surface which in turn increases the ionization of neutral atoms and thereby decreases the neutral atoms available for accretion. Since, the neutral atoms available for accretion decreases, the thickness of GS decreases on nitrogen doping. Moreover, the etching effect by nitrogen is additionally considered as the basis for decrease of thickness of nitrogen doped GS. The results of figure 1 are in consistence with the experimental observations of Seo et al. [1].
Figure 1. Variation of normalized thickness (in nm) of the undoped GS and nitrogen doped GS.

Using the above result, the field enhancement factor $\beta \approx \left( \frac{\lambda_{er}}{\tau_{er}} \right)$ is calculated using the saturated value of thickness corresponding to undoped and nitrogen doped GS. Since height $\lambda_{er}$ has little influence on the field enhancement factor [10], it is assumed to be 1 $\mu$m for the calculation of $\beta$ for undoped and nitrogen doped GS. It is found that the field enhancement factor is higher for nitrogen doped GS in comparison to undoped GS (cf. figure 2). The high field enhancement factor $\beta$ of nitrogen doped GS is due to reduced thickness of GS upon nitrogen doping. The similar observation has been reported by Takeuchi et al. [6] and Palnitkar et al. [7].

Figure 2. Field enhancement factor of undoped GS and nitrogen doped GS.

Acknowledgements
This work is partially supported by the Department of Science and Technology, Government of India.

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