Formalism to Study the Effect of Hydrogen on the Plasma-Assisted Growth and Field Emission Properties of the Graphene sheet

N. Gupta[1], S. C. Sharma[1], and R. Gupta[1]

[1]*Department of Applied Physics, Delhi Technological University (DTU),ShahbadDaulatpur, Bawana Road, Delhi-110042, India.*

Abstract

The catalytic growth of graphene grown via plasma enhanced chemical vapor deposition depends significantly on hydrogen in the feed gas. The effect of hydrogen on the dimensions of graphene has been investigated through a theoretical model that incorporates the charging rate of the graphene sheet; number density of all the plasma species, i.e., electrons, positively charged ions, and neutral atoms; and the growth rate of the graphene sheet. The numerical calculations have been carried out for typically glow discharge parameters and it is found that the thickness and height of the graphene sheet decreases with increase of the hydrogen gas density. Using the results obtained, the effect of hydrogen on the field emission properties of the graphene sheet has been proposed. It is found that the field enhancement factor β increases with the increase of hydrogen gas density. Some of the results of the present investigation are in accordance with the existing experimental observations. The results of the present model can serve as a major tool in analyzing the field emission characteristics of the graphene sheet.

I .Introduction

Hydrogen plays a dual role in the PECVD growth of graphene sheet (GS).It acts as an activator for the dissociation of hydrocarbon species into more active species and also as an etching reagent of graphene [1]. Thus, hydrogen gas number density profile plays a significant role on the growth of carbon nanostructures. The growth rate of carbon nanostructures decreases with the increase of hydrogen gas number density [2]. The number of layers of GS also get affected by the hydrogen gas number density [3] and thus the field enhancement factor which depends on the geometry of emitter [4] also get affected by the hydrogen gas density [5].

II. Model

The present model considers the growth of GS in the plasma consisting of electrons, positively charged ions and neutrals of CH_4 (denoted as A) and H_2 (denoted as B). The GS is formed due to following processes: (a) fragmentation of catalyst film into catalyst nanoparticles, (b) nucleation of carbon clusters, (c) diffusion and collision of these carbon clusters to form graphene islands (of radius a_{gh} = 50 nm), (d) formation of vertical GS on account of stress developed due to coalescence of graphene islands.

A. Growth rate equation for the graphene sheet

$$l\frac{d(\lambda\times\tau)}{dt}=\left(\left(\left(\frac{\eta_A}{\nu}\times\Lambda_1 e^{\left(-\left\{\frac{\varepsilon_d+\varepsilon_{in}}{k_B T_s}\right\}\right)}\right)\frac{\pi a_{gh}^2}{2\pi a_{gh}}\times\left(j_{iAghn}\right)+\left(\beta_{CH_4} j_{CH_4ghn}\right)\right)\times\frac{\mu_{ghn}}{\rho_{ghn}}, \quad (1)$$

$$\left[\lambda(t)\times l\right]\frac{d(\tau)}{dt}=\left\{\phi_{iA} e^{\left(\frac{-\delta E_{tdh}}{k_B\theta_{su}}\right)}+\phi_{iB}(1-\alpha_t)+\phi_{iB}+\alpha_{CH}\left(\phi_{iB}p_d+\gamma_0\nu e^{\left(\frac{-\delta E_i}{k_B\theta_{su}}\right)}\right)\right\}\frac{\lambda(t)}{\eta_{iB}}+\beta_{CH_4}\pi a_{gh}^2 j_{CH_4ghn}, \quad (2)$$

where *l*, λ and τ denote the length, height and thickness of the GS, respectively, η_A and η_{iB} are the number density of neutral A and ion B, respectively, μ_{ghn} is the mass of the growing GS and ρ_{ghn} is the density of the GS [6].

Eq.(1) describes the increase in area of the GS on account of diffusion and attachment of carbon atoms at the graphene island boundaries and ion (j_{iAghn}) & neutral (j_{CH4ghn}) collection current at the growing GS [6]. Eq. (2) depicts the decrease in thickness of the GS due to the etching effect of hydrogen [6].

B. Kinetic equation of positively charged ion density and neutral atoms

$$\frac{d\eta_{ik}}{dt}=\kappa_k\eta_k-\delta_A\eta_e\eta_{ik}-\eta_{ghn}j_{ikghn}-\psi_{adik}+\psi_{dpik} \quad (3)$$

$$\frac{d\eta_k}{dt}=\delta_k\eta_e\eta_{ik}-\kappa_k\eta_k+\eta_{ghn}\left(1-\beta_{ik}\right)j_{ikghn}-\eta_{ghn}\beta_k j_{kghn}, \quad (4)$$

where η_{ik} and η_k are the number density of ion and atom, respectively *(k* refers to A or B type of species), and η_e is the electron number density.

The Eq. (3) describes the kinetics of positively charged ions in the plasma due to ionization of neutral atoms (κ_k is the coefficient of ionization), recombination of electrons and ions (δ_k is the coefficient of recombination of electrons and ions), ion collection current at the GS surface, adsorption (ψ_{adik} is the adsorption flux) and desorption of ions (ψ_{dpik} is the desorption flux), and loss to the discharge wall. The term ψ_{thdh} represents the flux of type 2 ion on account of thermal dehydrogenation [6]. This term would not be accounted for the kinetics of positively charged ion density of type A.

The Eq. (5) describes the kinetics of neutral atomsin the plasma due to recombination of electrons and ions, ionization of neutral atoms, ion and neutral collection current at the GS surface.

RESULTS AND DISCUSSION

We have carried out calculations to study the effect of hydrogen number density on the growth and field emission properties of the GS for typically glow discharge parameters such as at t = 0; $\eta_{e0} = 10^9 cm^{-3}$, $\eta_{e0} = 0.6\eta_{iA0}$, $\eta_{A0} = 10^{10} cm^{-3}$, and $\beta_{ik} = \beta_k = 1$. In the present investigation, we have varied the number densities of hydrogen gas and have studied its repercussion on the dimensions (i.e., thickness and height) and field enhancement factor β of GS.

Fig.1 and 2 illustrate the variation of thickness and height of GS with time for different number density of hydrogen species in the plasma, respectively. From Fig.1 it can be seen that the thickness of the GS decreases with increase of the hydrogen number density. This is due to the augmentation of the etching of carbon atoms with increase of the hydrogen gas number density. It can be seen from Fig.2 that the height of the GS decreases with increase of the hydrogen gas number density. This is ascribed to the fact that on increasing the hydrogen gas density, the number density of carbon species decreases, and therefore the carbon species available for growth of height of GS get reduced. The similar observation has also been reported earlier for other carbon-based nanostructures [2].

Using the above results, the field enhancement factor $\beta = \lambda / \tau$ is calculated using the saturated value of λ and τ corresponding to different number densities of H_2 gas from Fig.1 and 2. It is found that the β increases with the augmentation of the hydrogen number density (cf. Fig.3). This result is due to the fact that height has little influence on β,[7] therefore, $\beta \propto 1/\tau$. Moreover, the thickness of GS decreases with the hydrogen gas number density (cf. Fig.1). Hence, β increases with increasing hydrogen number density. The results of Fig.1 and 3 are in compliance with the experimental observations of Chan *et al*. [4] and Malesevic *et al.*[7],respectively.

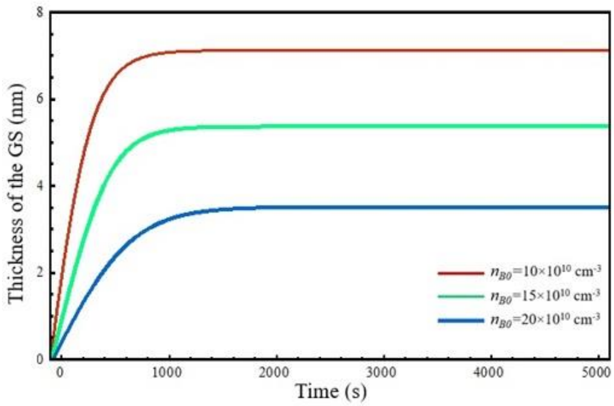

Fig.1. Time evolution of thickness of the graphene sheet for different number density of the hydrogen species in the plasma.

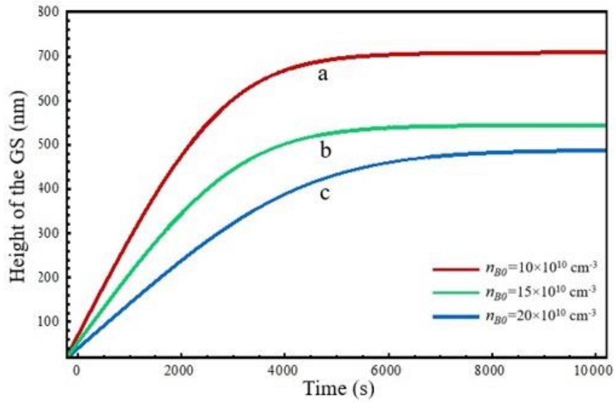

Fig.2. Time evolution of height of the graphene sheet for different number density of the hydrogen species in the plasma.

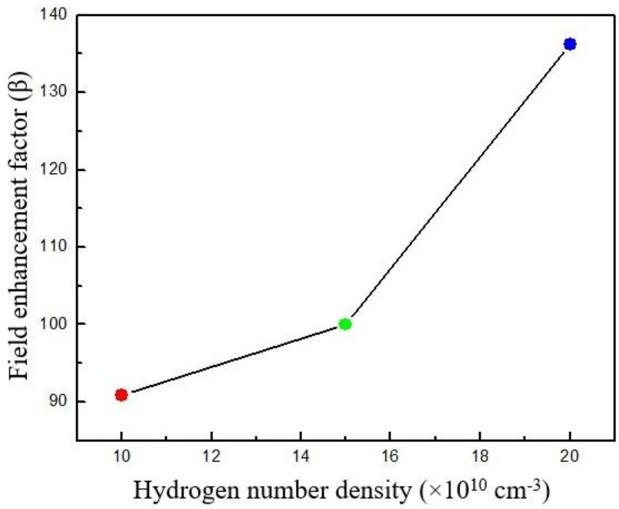

Fig.3. Variation of field enhancement factor of the GS with hydrogen species number density in the plasma.

References

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

[2] Vanpaemel J,van der Veen M H,Cott D J, Sugiura M,Asselberghs I,Gendt S De, and Vereecken P M 2015 J. Phys. Chem. C **119** 18293

[3]Denysenko I, and Ostrikov K 2007 Appl. Phys. Lett. **90** 251501

[4] Chan S H, Chen S H, Lin W T, Li M C, Lin Y C, and Kuo C-C 2013Nanoscale Res. Lett. **8** 28

[5]Kim Y, Song W, Lee S Y, Jeon C, Jung W, Kim M, and Park C-Y 2011 Appl. Phys. Lett. **98** 263106.

[6] Sharma S C and Gupta N 2015, Phys. Plasmas **22** 123517

[7] Malesevic A, Kemps R, Vanhulsel A, Chowdhury M P, Volodin A, andHaesendonck C V 2008 J. Appl. Phys. **104** 084301