Methane dissociation process in inductively coupled Ar/H₂/CH₄ plasma for graphene nano-flakes production

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The role of hydrogen and methane dissociation process in induction plasma synthesis of graphene nano-flakes (GNF) is studied by the optical emission spectroscopy of Ar/H₂/CH₄ plasma. The condensation of C₂ species formed due to methane decomposition produces GNF, which depends on pressure. Electron impact and dehydrogenation processes dissociate methane, which promotes and hinders the GNF production, respectively. The effect of hydrogen is insignificant on quality, size and morphology of the GNF. The CH₄ flow rate has no influence on particle temperature but has effect on cooling rate at the point of nucleation and, therefore, on production rate and thickness of GNF. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4977568>]

Graphene has attracted significant attention due to its remarkable physical and chemical properties and enormous potential for different applications.^{1–4} Many different techniques have been employed to synthesize graphene such as chemical vapour deposition (CVD),^{2–4} epitaxial growth,⁵ exfoliation method,¹ reduction of graphene oxide,⁶ inductively coupled thermal plasma (ICP) torch system,⁷ etc. Among the aforementioned techniques, the ICP torch system has been emerged as a suitable method for the synthesis of a wide variety of nanopowders.^{7–10} Electrodeless operation of the ICP torch in inert gas atmosphere involves clean plasma ensuring high purity products.¹¹ Carbon containing gaseous precursors have been employed for the synthesis of different carbon structures using various techniques by several research groups.^{2,4,12–14} Pristavita *et al.*¹² have used methane precursor for the synthesis of carbon nano-flakes by an ICP torch system for catalyst applications. A mixture of methane and hydrogen has also been used to grow multiwall carbon nanotubes in an ICP reactor.¹³ Vlassiounk *et al.*² have reported that hydrogen plays dual role as a cocatalyst and an etchant in thermal CVD growth of graphene using methane as carbon source. In the plasma enhanced CVD process, the role of hydrogen and the methane dissociation mechanism in plasma have not been discussed in detail although the mixture of argon, hydrogen and methane (Ar/H₂/CH₄) has widely been used for graphene synthesis.^{14–16} Moreover, the Ar/H₂/CH₄ plasma in radio frequency (RF) ICP torch system has not been diagnosed to understand the dissociation process for graphene synthesis. In this paper, we present the synthesis process of multi-layer graphene nano-flakes (GNF) with the in-situ investigation of Ar/H₂/CH₄ plasma by optical emission spectroscopy (OES) in an RF ICP reactor. The methane decomposition is governed primarily by electron impact and dehydrogenation process. The role of H₂ is found to be insignificant on quality, size and morphology of the synthesized GNF, which is in contrast to the thermal CVD growth of graphene.² Furthermore, production rate (PR) is

reduced with the addition of H₂ indicating that electron impact dissociation promotes whereas dehydrogenation hinders the production.

An RF ICP reactor was used to synthesize GNF comprising an ICP torch coupled to an RF power supply, a vacuum synthesis chamber, a filtration unit, a gas manifold, a flow control system and a precursor injector. The details about the RF ICP apparatus with schematic diagram can be found elsewhere.^{8–10} Following gas streams were used for the operation of the ICP torch to synthesize GNF: central gas [Ar (12 slpm)], sheath gas [Ar (60 slpm) + H₂ (0–8 slpm)] and reactive gas [Ar (3 slpm) + CH₄ (0.7–2 slpm)]. Pressure was varied from 400 to 700 mbar and the plate power with 45% coupling efficiency is fixed at 15 kW during the experiment.

OES measurement was conducted at different growth conditions using a fiber coupled spectrometer and collecting optics through a view port located at the distance of 115 mm from the exhaust of the ICP torch. Emission spectra were recorded in a time integrated manner and spatially averaged over 5 cm² area of the plasma. The synthesized nano-flakes were collected at a small bypass membrane filter of the filtration unit and characterized by scanning transmission electron microscopy (STEM), X-ray diffraction (XRD) and Raman spectroscopy.

The synthesis process involves the following sequences of gas flow into the ICP reactor chamber: (i) central, sheath and reactive carrier Ar gas with total flow rate (FR) of 75 slpm, (ii) addition of H₂ at varying FR of 0–8 slpm to the sheath Ar gas, and (iii) introduction of reactive CH₄ precursor gas at varying FR of 0.7–2 slpm. The emission spectra shown in Fig. 1 of pure Ar plasma [sequence (i)] at 400 mbar are dominated by neutral argon (Ar I) transitions, which are identified using Ref. 17. Inset (a) of Fig. 1 shows the Ar plasma emission below 690 nm. The Ar plasma temperature (T_{Ar}) is estimated to be 6050 K from the slope of the Boltzmann plot [inset (b) of Fig. 1] of $\ln(I_{ki}\lambda_{ki}/g_k A_{ki})$ versus E_k using spectral response corrected Ar I emission lines under the assumption of local thermodynamic equilibrium (LTE).^{18,19} The electron density (n_e) is calculated by considering the Stark broadening mechanism in plasma and is

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FIG. 1. Ar and Ar/H₂ plasma emission spectra at 400 mbar. Insets (a) and (b) show Ar plasma emission between 400 and 690 nm and the Boltzmann plot of $Y(= \ln(I_k \lambda_k / g_k A_k))$ versus E_k , respectively.

related to the half-width ($\Delta\lambda_{1/2}$) of Stark-broadened line as $\Delta\lambda_{1/2} = 2W(n_e/10^{16}) \text{ \AA}$, where W is the electron impact parameter.¹⁸ Since the Stark broadening exhibits Lorentzian profile, the Ar I transition at 696 nm is fitted using the Voigt function to determine the Lorentzian linewidth to estimate n_e , which is found to be $\sim 10^{18} \text{ cm}^{-3}$ in Ar plasma.

H₂ gas with FR of 4 slpm is then introduced into the existing Ar plasma at 400 mbar [sequence (ii)]. The emission spectrum of Ar and H₂ mixture (Ar/H₂) plasma is shown in Fig. 1, which contains atomic hydrogen lines at 656 (H _{α}) and 486 nm (H _{β}), and Ar I transitions above 690 nm with reduced intensity compared to sequence (i). The Ar/H₂ plasma temperature ($T_{\text{Ar/H}_2}$) is determined using the intensity ratio of the H _{α} and H _{β} lines²⁰ and is found to be 4210 K. The electron density (n_e) in Ar/H₂ plasma is estimated to be $\sim 10^{15} \text{ cm}^{-3}$ by considering the H _{β} line and using the corresponding formula:^{21,22} $\log n_e = 1.452 \log(\Delta\lambda_L) + 16.017$, where $\Delta\lambda_L$ is the Lorentzian linewidth of H _{β} line. Both electron density and temperature are reduced with the admixing of H₂ in Ar plasma, which is consistent with the reduction in plasma intensity, as shown in Fig. 1. This can be understood by considering the following reactions:²³

The addition of H₂ reduces the degree of ionization of the Ar plasma resulting in neutral Ar gas and excited state hydrogen

atoms (H*) due to the combined effect of reactions (1) and (2). Thus, we have observed dominant H _{α} line along with the H _{β} transition in the emission spectrum of Ar/H₂ plasma (Fig. 1). Furthermore, the diffusion of hydrogen is fast in hydrogen containing plasma and atomic hydrogen is known to have large adsorption rate on metal surfaces.²⁴ Therefore, the adsorption of H atoms produced in Ar/H₂ plasma can take place on the walls of the reactor. Subsequently, the gaseous phase H atoms can combine with the H atoms adsorbed on the walls of the reactor to form the vibrationally excited H₂ molecules (H₂*). Consequently, reaction can occur between H₂* and hydrogen ions as follows:²³

H₂⁺ can further dissociate to produce H and H* according to the following reaction:

Reactions (2) and (4) suggest that the appearance of H _{α} and H _{β} emissions in Fig. 1 is based on decrease in n_e in Ar/H₂ plasma, which is in agreement with our experimental observation. The reduction in temperature from $T_{\text{Ar}} = 6050 \text{ K}$ to $T_{\text{Ar/H}_2} = 4210 \text{ K}$ could be attributed to the reentry flow of H₂* into the expanding plasma, which has been considered to be responsible for the fast ionization loss in plasma.²³

In sequence (iii), CH₄ gas at FR of 0.7 slpm is injected axially into the existing Ar/H₂ plasma in the reactor. Figure 2(a)

FIG. 2. Ar/H₂/CH₄ plasma emission spectra at different (a) pressures at H₂ and CH₄ FR of 4 and 0.7 slpm, respectively, (b) CH₄ FRs at 700 mbar and H₂ FR of 4 slpm, and (c) H₂ FRs at 600 mbar and CH₄ FR of 0.7 slpm. The insets of (a) and (b) show the plot ($\blacksquare$) between $G(\nu)$ and $Y(= \ln(\sum_{\nu'} (\lambda^4 I_{\nu'})))$ at 400 mbar and semi-logarithmic plot ($\blacksquare$) of $Y(= \ln(\sum_{\nu'} (\lambda^4 I_{\nu'})))$ against $1/\lambda$ at CH₄ FR of 1.1 slpm, respectively. The solid line in the insets is the linear fit. The inset of (c) shows the STEM images of GNF at H₂ FR of 0 and 4 slpm.

shows the emission spectra of Ar/H₂/CH₄ plasma that are dominated by the C₂ swan system at and below 600 mbar. No Ar I transitions are evident and H_α emission is negligibly small. The different observed transitions marked by **1–9** are assigned based on their spectral positions. The bands **4**, **5**, **6**, **7**, and **9** represent C₂ swan system occurring at about 436, 468, 516, 563 and 619, respectively, corresponding to the vibration sequences $\Delta\nu = +2, +1, 0, -1, -2$ of the ($d^3\Pi_g - a^3\Pi_u$) electronic transitions. The emissions **1**, **2**, **3** and **8** at 387, 405, 431 and 612 nm, respectively, are attributed to the emissions from CH($B^2\Sigma^- \rightarrow X^2\Pi$), C₃, CH($A^2\Delta \rightarrow X^2\Pi$) and H₂.^{25,26} The formation of C₂, C₃, and CH radicals indicates that electron impact and the dehydrogenation processes are responsible for the dissociation of CH₄ due to the presence of both electrons and atomic hydrogens in the plasma.²⁵ The C₂ transitions observed in the Ar/H₂/CH₄ plasma arise due to the energy transfer from Ar* to C₂H₂ and/or C₂H formed during the dissociation of CH₄.²⁷ Goyette *et al.*²⁸ have reported that the C₂ swan band head emission intensity corresponding to $\Delta\nu = 0$ at 516 nm correlates linearly with C₂ density. We have observed a decrease in C₂ emission intensity with an increase in pressure [Fig. 2(a)], which indicates a decrease in C₂ concentration. The formed C₂ species in Ar/H₂/CH₄ plasma can be depleted due to the formation of hydrocarbons by collision with the hydrogen molecules through the reaction:^{26,29} $C_2 + H_2 \rightarrow C_2H + H$. Moreover, C₂ exists only in a gaseous state that can condense to form different allotropes of carbon, as the temperature is sufficiently lowered. The C₂ vibrational temperature (T_{C_2}) is estimated by analyzing the C₂ swan band emission intensities ($I_{\nu\nu'}$) using the following relation based on LTE:^{30,31} $\ln\left(\sum_{\nu'}(\lambda^4 I_{\nu\nu'})\right) = C_1 - G(\nu)(hc/k_B T_{C_2})$. The meanings of the symbols are reported elsewhere.³¹ The inset of Fig. 2(a) shows a typical example of plot between $G(\nu)$ and $\ln\left(\sum_{\nu'}(\lambda^4 I_{\nu\nu'})\right)$ represented by the solid squares (■), and the solid line is the linear fit yielding $T_{C_2} = 4060 \pm 180$ K at 400 mbar. T_{C_2} is found to be decreased from 4060 to 3520 K with an increase in pressure from 400 to 700 mbar. At lower pressures, the expanding plasma experiences less obstruction. So, the plasma species remain highly energetic. At sufficiently high pressures, substantial collision with the species of the ambient results in slowing down of the plasma expansion inducing rapid cooling of plasma and initiation of chemical reactions.^{32,33} Chemical reactions generate monomers that lead to particle nucleation upon sufficient cooling and formation of nanoparticles due to the condensation of supersaturated

vapor.³⁴ At 400 mbar, no particles are formed indicating that the saturation ratio is not high enough due to lower thermal gradient in plasma (∇T).³⁴ So, the C₂ species form hydrocarbon that then flows out of the reaction zone without producing any allotropes of carbon.^{26,29} The PR of collected powder is ~ 1 and 16 mg/min at 600 and 700 mbar, respectively, betokening that the saturation ratio is high enough to favor particle nucleation due to higher ∇T caused by enhanced collisions with an increase in pressure. Thus, the decrease in C₂ density with an increasing pressure is associated with conversion from gaseous to condensed phase. A broad band continuum emission marked by the arrow in Fig. 2(a) is predominantly observed in the Ar/H₂/CH₄ plasma emission spectrum at 700 mbar, which is attributed to the emission from the nanoparticles formed in condensed phase and is consistent with the powder production. At higher CH₄ FR (1.1–2 slpm), the continuum emission dominates the spectra at 700 mbar, as shown in Fig. 2(b). Particle temperature (T_p) can be estimated by considering the continuum emission as Planck's radiation spectrum since hot nanoparticles behave as black-body radiator and using the relation for emission intensity (I) given by³⁵ $I(\lambda) \propto \lambda^{-5} \exp\left(-\frac{hc}{\lambda k_B T_p}\right)$. The inset of Fig. 2(b) shows a schematic semi-logarithmic plot of ($I\lambda^5$) against ($1/\lambda$) obtained from the spectral response corrected continuum emission observed in the Ar/H₂/CH₄ plasma, and the solid line is the linear fit that gives T_p of 2220 ± 30 K at 700 mbar and CH₄ FR of 1.1 slpm. The variation of T_p is negligibly small with CH₄ FR, i.e., 2180 ± 50 and 2260 ± 50 K at CH₄ FR of 1.5 and 2 slpm, respectively. Since the C₂ species condense to form particles at the boundary of the expanding plasma and CH₄ is injected on the axis of plasma, increasing CH₄ FR does not have influence on T_p . Thus, the increase in continuum emission intensity with increasing CH₄ [Fig. 2(b)] is attributed to the increasing condensation of C₂ species to form particles. As a result, PR is expected to increase with an increase in CH₄. However, PR is initially increased from ~ 16 to 100 mg/min with an increase in CH₄ from 0.7 to 1.5 slpm and then decreases to ~ 50 mg/min at 2 slpm at 700 mbar. In order to understand such discrepancy, the STEM images and XRD spectra of the collected powder are analyzed. Figure 3 shows the representative STEM images, XRD and Raman spectra at 700 mbar for 1.5 and 2 slpm of CH₄. The synthesized powders exhibit the flake-like structures having length and width approximately 200 and 100 nm, respectively. The diffraction peaks at $2\theta = 26^\circ, 43^\circ, 54^\circ$ and 78° correspond to the (002), (100), (004) and (110) planes of the graphitic structure, respectively. The planes (100) and (110) are the

FIG. 3. STEM images, XRD and Raman spectra of GNF at 700 mbar and H₂ FR of 4 slpm for CH₄ FRs of 1.5 and 2 slpm.

characteristics of the 2D in-plane symmetry along the graphene layers.³⁶ The thickness of GNF is estimated using the Scherrer formula, and the layer-to-layer distance (d_{002}) between two successive graphene layers is calculated by considering the peak position of the (002) plane.³⁷ The number of layers in each GNF sample is determined by using the values of corresponding thickness and d_{002} .³⁶ The thickness of the nano-flakes is found to be ~ 4 nm at 700 mbar for CH_4 FR ≤ 1.5 slpm, whereas at CH_4 FR of 2 slpm, thickness is 7.5 nm. The number of layers of the GNF at 700 mbar is about 11–12 for CH_4 FR ≤ 1.5 slpm and 22 for CH_4 FR of 2 slpm. The observation of higher thickness of nano-flakes with lower PR at 700 mbar for CH_4 FR of 2 slpm is associated with the formation of higher monomer concentration and lower cooling rate at the point of nucleation due to higher ∇T caused by excessive CH_4 flow on the axis of plasma.^{12,34} The main features observed in the Raman spectra are D band at 1345 cm^{-1} , G band at 1577 cm^{-1} and 2D band at 2688 cm^{-1} .³⁶ The intensity ratio of D and G band (I_D/I_G), a measure of the quality of the material, is found to be about 0.3 at 700 mbar for all CH_4 FRs, indicating good quality of the GNF. The observed higher intensity of 2D band than G band could be associated with the presence of disclinations.³⁸

The $\text{Ar}/\text{H}_2/\text{CH}_4$ plasma emission spectra are recorded at 600 mbar and 0.7 slpm CH_4 FR for different H_2 FRs of 0, 4 and 8 slpm, as shown in Fig. 2(c), which contain the transitions described in Fig. 2(a). In the absence of H_2 , CH_4 is initially decomposed by electron impact that produces atomic hydrogen. Subsequently, dehydrogenation takes part in the dissociation process. The addition of H_2 decreases electron density in plasma,²³ which encumbers the electron impact dissociation, and at higher H_2 FR, dehydrogenation process dominates. Thus, the observed higher C_2 emission intensity at H_2 FR of 8 slpm is attributed to the dominating effect of dehydrogenation process. Intermediate behavior is observed for H_2 FR of 4 slpm. T_{C_2} is found to be decreased from 5090 to 3390 K with increasing addition of H_2 , i.e., from 0 to 8 slpm which is consistent with $T_{\text{Ar}/\text{H}_2} < T_{\text{Ar}}$.

The higher C_2 density observed at H_2 FR of 8 slpm with reduced T_{C_2} is expected to lead more production; however, no production is observed. Moreover, PR is found to be decreased with addition of H_2 , i.e., 20, 1 and 0 mg/min for H_2 FR of 0, 4 and 8 slpm, respectively. This indicates that the addition of H_2 promotes the formation of hydrocarbons that encumbers the condensation of C_2 species to produce GNF. The GNF collected for H_2 FR of 0 and 4 slpm are characterized by STEM, XRD and Raman spectroscopy. The STEM images at 600 mbar shown in the inset of Fig. 2(c) indicate similar length and width as that of 700 mbar and no significant influence of H_2 on morphology of the GNF. The XRD analysis reveals that the thickness (~ 4 nm) of the GNF is also not affected by the addition of H_2 , which is in contrast to the thermal CVD growth of graphene.² The I_D/I_G ratio from the Raman spectra is found to be 0.4 and 0.3 for H_2 FR of 0 and 4 slpm, respectively.

In summary, we have investigated the dissociation process of methane with *in-situ* monitoring of $\text{Ar}/\text{H}_2/\text{CH}_4$ plasma in an RF ICP reactor by OES. The GNF production is observed at higher pressure due to the condensation of C_2 species. The increasing CH_4 FR has no influence on T_p but

affects ∇T resulting in an increase in PR up to 1.5 slpm and a decrease in PR above 1.5 slpm. The addition of H_2 decreases the PR betokening that electron impact dissociation process is responsible for GNF production and dehydrogenation hinders the production. Moreover, the effect of hydrogen is found to be insignificant on quality, size and morphology of the GNF. This study will be helpful to optimize the growth parameters in different plasma based synthesis techniques to produce quality graphene and its derivatives.

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