Optical emission spectroscopic study of Ar/H₂/CH₄ plasma during the production of graphene nano-flakes by induction plasma synthesis

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Abstract. Graphene nano-flakes using CH₄ precursor were synthesized in a radio frequency inductively coupled plasma reactor with in-situ investigation of Ar/H₂/CH₄ plasma by optical emission spectroscopy at fixed H₂ and Ar flow rates of 4 and 75 slpm, respectively, and at different plate powers (12 to 18 kW), pressures (400 to 700 mbar) and CH₄ flow rates (0.3 to 2 slpm). Emissions from C₂ Swan band, C₃, CH and H₂ are observed in the optical emission spectra of Ar/H₂/CH₄ plasma. Plasma temperature estimated analyzing the C₂ Swan band emission intensities is found to be decreased with increasing pressure and decreasing plate power. The decreasing plasma temperature gives rise to increase in production rate due to increase in condensation process. The production rate is observed to be increased from 0 to 0.3 g/h at 18 kW and from 0 to 1 g/h at 15 kW with increase in pressure from 400 to 700 mbar at fixed CH₄ flow rate of 0.7 slpm. Broad band continuum emission appears in the emission spectra at specific growth conditions in which the formation of vapor phase nanoparticles due to condensation of supersaturated vapor is facilitated. The production rate at 12 kW, 700 mbar, and 0.7 slpm of CH₄ flow rate is found to be 1.7 g/h which is more than that at 15 and 18 kW. Thus, the broadband continuum emission dominates the optical emission spectra at 12 kW due to lower temperature and higher production rate, and is attributed to the emission from suspended nanoparticles formed in vapor phase. The synthesized nanoparticles exhibit flake like structures having average length and width about 200 and 100 nm, respectively, irrespective of the growth conditions. Nano-flakes have thickness between 3.7 to 7.5 nm and are composed of 11 to 22 graphene layers depending on the growth conditions. The intensity ratio (I_D/I_G) of D and G band observed in the Raman spectra is less than 0.33 which indicates good quality of the synthesized graphene nano-flakes.

1. Introduction
Synthesis of nanoparticles has been gained significant attention due to remarkably different physical and chemical properties of nanoparticles from their bulk counterpart in spite of possessing the same constituents [1, 2]. Many different techniques have been employed to synthesize various nanoparticles for different applications. The commonly used synthesis methods are colloidal chemistry, sol-gel methods, laser ablation and photochemical synthesis [3, 4]. Nanoparticles synthesized using chemical routes are not contaminate free due to the presence of other ions and reaction products from the reducing reactions [4]. Laser ablation synthesis process produces contaminant free high purity nanoparticles since nanoparticles are formed due to condensation of laser ablated plasma from a high purity target material and it does not involve chemical reagents in solutions [3, 4]. However, laser ablation technique cannot produce high quantity of nanoparticles at low cost for industrial applications. Radio frequency (RF) inductively coupled plasma (ICP) synthesis technique is an alternative plasma route for the synthesis of nanoparticles which is better than conventional plasma due to a large volume, high-temperature plasma zone, operating under different atmospheres, permitting synthesis of a great variety of nanoparticles, higher production rate with lower processing cost [5]. Furthermore, electrodeless operation of the ICP torch in the inert gas atmosphere involves clean plasma that ensures synthesis of high purity products [6]. Thus, RF thermal plasma is suitable for
industrial scale mass production of high purity materials as it is a continuous process to accomplish high production volume with good synthesis control from the gaseous phase. A wide range of nanoparticles has been produced using appropriate precursors in RF inductively coupled plasma reactor [7-10]. In RF ICP synthesis system, the injected precursors convert into plasma which comprises mainly of electrons, ions and neutrals, and are the main source of the nanoparticles. Thus, it is imperative to characterize the plasma of the precursor during the synthesis of nanoparticles. Optical emission spectroscopy (OES) is a sensitive and non-invasive in-situ investigation technique to probe different constituents of plasma which provides useful information on different excited states in the plasma [11]. A detailed analysis of the emission lines observed at different spectral positions in the optical emission spectra reveals some important characteristics of the investigated plasma. The instrumentation associated with the OES study of plasma is very simple and straightforward which mainly involves simple optics to collect light emission from the plasma and a spectrometer to record the emission spectra. Plasma produced by several methods has been characterized by OES for different applications [12-15]. Ma et al. [12] have conducted OES measurements to investigate the microwave activated Ar/H2/CH4 plasma during the chemical vapor deposition of polycrystalline diamond. They have monitored the emissions from electronically excited H and Ar atoms, and C2 and CH radicals as function of Ar and CH4 flow rates, input power and pressure, and proposed that different species have different formation mechanisms since they exhibit different behaviors. Zhou et al. [13] have performed OES study and reported the existence of abundant C2 and CH species in CH4/Ar plasma along with C3 species and/or 4-carbon clusters. They attributed CH radicals to be responsible for the trans-polyacetylene composition in the grain boundaries of deposited nano-crystalline diamond film. In recent years, synthesis of high quality graphene structures has been received increasing attention due to its distinct properties and potential applications in nanoelectronics [16]. Several studies have been reported on the synthesis of graphene nano-flakes with theoretical modelling based on fundamental theory and CFD calculations [17, 18]. However, systematic analysis of the synthesis process in RF ICP system with in-situ investigation of plasma to understand the dissociation process of precursor has not been discussed in detail. In this study, we have done extensive in situ investigation of RF inductively coupled Ar/H2/CH4 plasma by OES in order to monitor the radicals formed due to dissociation of CH4 during the synthesis process of the graphene nano-flakes. Emission spectra of Ar/H2/CH4 plasma are dominated by the emission from C2 Swan system. Optical emissions from CH (B2Σ+ → X2Π), C3, CH (A2Δ → X2Π) and H2 are also observed. The variation of plasma and particle temperatures with different growth conditions are compared with that of production rate. The properties and quality of the synthesized graphene nano-flakes are cognized by electron microscopy, x-ray diffraction and Raman spectroscopy. The synthesized nano-flakes have uniform morphology having average length and width about 200 and 100 nm, respectively. The thickness of the nano-flakes is found to be between 3.7 to 7.5 nm, and the number of graphene layers varies from 11 to 22 depending on the growth conditions. The intensity ratio (I_D/I_G) of D and G band observed in the Raman spectra is less than 0.33 which betokens good quality of the synthesized graphene nano-flakes.

2. Experimental details

Figure 1 shows a schematic diagram of the RF inductively coupled thermal plasma facility developed at EMPA in Thun, Switzerland for the synthesis of nanoparticles. It comprises of an induction plasma torch coupled to a RF power supply, a vacuum synthesis chamber, a filtration unit, a gas manifold, a flow control system and a precursor injector. The plasma torch (PL-35, TEKNA Plasma System Inc. Canada) mounted on the top of the synthesis chamber is connected to a RF power supply (Elgotec AG, Switzerland) delivering a maximum electrical power of 35 kW at a frequency of 13.56 MHz. The plate power was varied from 12 to 18 kW in this experiment. The plasma torch consists of a four turn induction coil, a water cooled 35 mm inner diameter ceramic tube, and another 30 mm outer diameter ceramic tube which separates the central gas from the sheath gas. The central gas was introduced tangentially through a metallic gas distributor with a swirl, whereas sheath gas was injected axially.
along the ceramic wall. More details about the RF ICP apparatus can be found elsewhere [7–9]. Argon (Ar) gas with fixed flow rate of 12 slpm was used as central gas, and a mixture of Ar and hydrogen (H\textsubscript{2}) gas with fixed flow rates of 60 and 4 slpm, respectively, as sheath gas. Gas precursor with carrier gas referred to as reactive gas was introduced axially into the induction plasma torch. Ar gas with fixed flow rate of 3 slpm was used as carrier gas, and methane (CH\textsubscript{4}) gas with varying flow rates (0.3–2 slpm) was used as precursor. Thus, the total flow rates of Ar and H\textsubscript{2} gas were fixed at 75 and 4 slpm, respectively, during the experiment.

The water cooled synthesis chamber was connected via a filtration unit to a water-ring pump with a pressure regulation system. The pressure was varied from 400 to 700 mbar in the experiment. The synthesis chamber was also equipped with view ports for the in-situ process visualization and characterization. Optical emission spectroscopy (OES) experiment was conducted at different growth conditions using a fiber coupled spectrometer (Ocean Optics) and collecting optics through a view port located at distance of 115 mm from the exhaust of the ICP torch. Each emission spectrum was recorded in time integrated manner and spatially averaged over 5 cm\textsuperscript{2} area of the plasma.

The filtration unit comprises of a small bypass membrane filter which was used for on-line sampling of the synthesized nanoparticles. Imaging of the synthesized nanoparticles were carried out by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) using a field emission microscope (Hitachi S4800 high-resolution SEM). The synthesized powders were pelletized (Ø.10 mm, thickness 1mm) for x-ray diffraction (XRD), and Raman spectroscopy characterization. XRD patterns were measured using a X-Ray Bruker D8-Discover diffractometer in Bragg–Brentano geometry. Confocal optical microscope system (NTEGRA Spectra) was used for Raman experiment. A 532 nm Nd:YAG laser with power of 10 mW was focused using a microscope objective onto the sample with a focal spot diameter of about 1 μm. The Raman scattered signal was recorded using a charge-coupled device (CCD) attached to a spectrometer in the back-scattered geometry.

Figure 1. Schematic diagram of RF inductively coupled thermal plasma apparatus developed at EMPA in Thun, Switzerland.

3. Results and discussion

Figure 2(a) shows the optical emission spectrum of Ar/H\textsubscript{2}/CH\textsubscript{4} plasma recorded at plate power of 18 kW, pressure of 400 mbar and CH\textsubscript{4} flow rate of 0.7 slpm. The observed emission bands are represented by a–i in the figure which corresponds to the wavelengths at 387, 405, 431, 436, 468, 516,
563, 612 and 619 nm, respectively. The C$_2$ Swan system corresponding to the vibration sequences \( \Delta \nu = +2, +1, 0, -1, -2 \) of the \((d^3\Pi_g - d^3\Pi_u)\) electronic transitions dominates the optical emission spectrum which are marked by d, e, f, g and i, respectively. The emissions a, b, c and h at 387, 405, 431 and 612 nm, respectively, are attributed to the emissions from CH$_2$(\( \Delta \nu = 0 \)) and H$_2$ [13, 19]. No Ar I transitions are evident and atomic hydrogen transitions including emission at 656 nm (H$_\alpha$) is negligibly small in comparison to the C$_2$ Swan band emissions. Different radicals in the emission spectra are appeared due to dissociation of CH$_4$. Electron impact and the dehydrogenation dissociations are the two primary mechanisms for the dissociation of CH$_4$ [20, 21].

The observed dominant emission bands in Ar/H$_2$/CH$_4$ plasma originating from C$_2$ Swan system can be analyzed to estimate the molecular vibrational temperature using the following relation [22, 23] which is based on local thermodynamic equilibrium (LTE) condition:

\[
\ln\left( \sum_{\nu'} \left( \lambda^2 I_{\nu \nu'} \right) \right) = C_1 - G(\nu) \frac{hc}{kT_{\text{vib}}} \tag{1}
\]

where \( \lambda \) is the wavelength corresponding to the emission, \( I_{\nu \nu'} \) is the Swan band emission intensity of the progression \((\nu \nu')\), \( h \) the Planck’s constant, \( c \) refers to the velocity of light, \( C_1 \) a constant, \( G(\nu) \) the term value corresponding to the vibrational level in the upper electronic state and \( T_{\text{vib}} \) the vibrational temperature. The slope of the linear plot between \( G(\nu) \) and \( \ln\left( \sum_{\nu'} \left( \lambda^2 I_{\nu \nu'} \right) \right) \) can provide the vibrational temperature which is a measure of plasma temperature under LTE. Figure 2(b) shows a schematic plot between \( G(\nu) \) and \( \ln\left( \sum_{\nu'} \left( \lambda^2 I_{\nu \nu'} \right) \right) \) represented by the solid squares (■), and the solid line is the linear fit which yields a temperature of 6200 K for the Ar/H$_2$/CH$_4$ plasma at plate power of 18 kW, pressure of 400 mbar, and CH$_4$ flow rate of 0.7 slpm.
At high plate powers above 15 kW, the C\textsubscript{2} Swan band emissions recorded at fixed CH\textsubscript{4} flow rate of 0.7 slpm dominate the optical emission spectra of Ar/H\textsubscript{2}/CH\textsubscript{4} plasma in the pressure range from 400 to 700 mbar. However, the intensity of the C\textsubscript{2} Swan band decreases with increase in pressure leading to the decrease in plasma temperature. The estimated plasma temperature decreases from 4060 to 3520 K at 15 kW as the pressure increases from 400 to 700 mbar. The decrease in plasma temperature with increase in pressure and decrease in plate power gives rise to the increase in condensation process of nanoparticles formation. Thus, the broad band continuum emission appears along with the C\textsubscript{2} Swan band in the optical emission spectra of Ar/H\textsubscript{2}/CH\textsubscript{4} plasma at 15 kW above 600 mbar which is attributed to the emission from nanoparticles formed in vapor phase. The production rate is found to be increased from 0 to 0.3 g/h at 18 kW and from 0 to 1 g/h at 15 kW as the pressure increases from 400 to 700 mbar.

Since the plasma temperature decreases and consequently, the production rate increases for a fixed pressure and CH\textsubscript{4} flow rate as the plate power decreases from 18 to 15 kW, the plate power is further reduced to 12 kW in order to see the effect of decreasing plasma temperature on the optical emission characteristics and the production rate at different pressures. The optical emission spectra of Ar/H\textsubscript{2}/CH\textsubscript{4} plasma at plate power of 12 kW and CH\textsubscript{4} flow rate of 0.7 slpm at all pressures are found to be dominated by the continuum emission from the nanoparticles, and the C\textsubscript{2} Swan band emission is negligible as shown in Fig. 3. The particle temperature is estimated from the spectral response corrected continuum emission following Ref. 24 which decreases from 2200 to 1700 K with increase in pressure from 400 to 700 mbar similar to the behavior of plasma temperature. The production rate is also increased with increase in pressure which is consistent with that of at 15 and 18 kW. In addition, the production rate is more at 12 kW than that at 15 and 18 kW for a fixed pressure and CH\textsubscript{4} flow rate due to increasing condensation of supersaturated vapor at lower temperature. The combination of lowest plate power (12 kW) and highest pressure (700 mbar) considered in this experiment yields higher production rate of 1.7 g/h than other combinations of plate powers and pressures at fixed CH\textsubscript{4} flow rate of 0.7 slpm. Thus, we varied the CH\textsubscript{4} flow rate at fixed pressure of 700 mbar and plate power of 12 kW in order to optimize the CH\textsubscript{4} flow rate to achieve maximum production rate. However, we could not conduct the experiment at 12 kW and 700 mbar at higher CH\textsubscript{4} flow rates than 0.7 slpm since the capacity to dissociate CH\textsubscript{4} and produce plasma was insufficient. Therefore, the plate powers were increased to 15 and 18 kW at 700 mbar and the production rate was monitored at different CH\textsubscript{4} flow rates. The production rate is found to be maximum at 1.5 slpm of CH\textsubscript{4} flow rate for both plate powers, and is 6 and 7 g/h at 15 and 18 kW, respectively.

![Figure 3](image_url)
The nanoparticles collected at the filter were characterized by SEM and STEM in order to understand the surface morphology. Figure 4 shows the representative SEM and STEM images of the nanoparticles which depicts uniform surface morphology. The nanoparticles exhibit flake like structures having average length and width of about 200 and 100 nm, respectively, irrespective of the growth conditions. Figure 5(a) shows the XRD spectrum of the nano-flakes synthesized at plate power of 18 kW, pressure of 700 mbar, and CH$_4$ flow rate of 0.7 slpm which is a representative spectrum for all growth conditions. The diffraction pattern shows the crystalline nature of the nano-flakes. Four diffraction peaks are identified at 2θ angles of 26°, 43°, 54° and 78°. The diffraction peaks at 2θ = 26° and 43° correspond to the (002) and (100) planes, respectively, which are the typical features of the graphitic structure and have been identified in XRD spectrum of graphene sheets. The peak at 2θ = 54° corresponds to the (004) plane parallel to the (002) plane at 2θ = 26° of the graphene layers. In addition, the diffraction lines at 2θ = 43° and 78° corresponding to the planes (100) and (110), respectively, are the characteristics of the 2D in-plane symmetry along the graphene layers [25]. The thickness of the graphene nano-flakes is estimated using the Scherrer formula, and the layer-to-layer distance ($d_{002}$) between two successive graphene layers is calculated using the peak position of the (002) plane [26]. The number of layers in each graphene nano-flakes sample is determined by using the values of corresponding thickness and $d_{002}$ [25]. The thickness of the nano-flakes is found to be between 3.7 to 7.5 nm and the number of layers in the synthesized graphene nano-flakes varies between 11 and 22 depending on the growth conditions.

![Figure 4. SEM (a) and STEM (b) images of the synthesized nano-flakes at plate power of 15 kW, pressure of 700 mbar and CH$_4$ flow rate of 0.7 slpm.](image)

![Figure 5. Representative XRD (a) and Raman (b) spectra of nano-flakes synthesized at plate power of 18 kW, pressure of 700 mbar and CH$_4$ flow rate of 0.7 slpm.](image)
Raman spectroscopy was used to evaluate the quality of the nano-flakes synthesized at different growth conditions. Figure 5 (b) shows a representative Raman spectrum of the synthesized nano-flakes at plate power of 18 kW, pressure of 700 mbar and CH$_4$ flow rate of 0.7 slpm. The main features observed in the Raman spectra of all samples are D band at 1345 cm$^{-1}$, G band at 1577 cm$^{-1}$ and 2D band at 2686 cm$^{-1}$. The D band at 1345 cm$^{-1}$ does not appear in pristine graphene and is observed where symmetry is broken by edges or in samples with a high density of defects [16, 27]. Since the average length and width of investigated graphene nano-flakes are about 200 and 100 nm, respectively, major contribution of edge effects to the D band intensity is expected. The intensity ratio of D and G band ($I_D/I_G$), a measure of the quality of the material, is found to be less than 0.33 in the synthesized graphene nano-flakes for all growth conditions. The smaller value of $I_D/I_G$ ratio (< 0.33) in spite of having contribution from edges to the D band intensity ensures high quality nano-flakes in our case. The variation of $I_D/I_G$ ratio with different growth conditions is also found to be negligibly small i.e. from 0.24 to 0.33 which indicates no influence of processing conditions on the quality of the synthesized graphene nano-flakes. Moreover, the synthesized graphene nano-flakes have smaller values of $I_D/I_G$ ratio in comparison to microwave plasma enhanced chemical vapor deposited graphene nano-flakes of similar width [28] which further ensures quality growth at low cost with higher production rate in the ICP synthesis system.

4. Conclusions

Graphene nano-flakes are synthesized by using RF ICP synthesis system at different growth conditions with in situ investigation of Ar/H$_2$/CH$_4$ plasma by optical emission spectroscopy. The C$_2$ Swan system corresponding to the vibration sequences $\Delta v = +2$, +1, 0, -1, -2 of the ($d^3\Pi_g - a^3\Pi_u$) electronic transitions dominates the optical emission spectra. The molecular vibrational temperature, a measure of plasma temperature, estimated by analyzing the C$_2$ Swan band emission intensities is found to be decreased with increase in pressure and decrease in plate power. The production rate is also increased with increase in pressure and decrease in plate power. Thus, the increase in production rate is associated with decrease in plasma temperature due to increasing condensation of supersaturated vapor. The broadband continuum emission appears in the optical emission spectra at certain growth conditions in which formation of vapor phase nanoparticles is facilitated. Thus, continuum emission acts as an indicator of the vapor phase nanoparticles formation. The maximum production rate of the graphene nano-flakes synthesized in current ICP apparatus is 7 g/h at plate power of 18 kW, pressure of 700 mbar and CH$_4$ flow rate of 1.5 slpm. The capacity of RF ICP synthesis system can further be improved to increase the production rate at lower processing cost. Higher plate power and pressure together with higher CH$_4$ flow rate could probably lead to higher production rate in the ICP synthesis system. The synthesized graphene nano-flakes have uniform morphology having average length and width about 200 and 100 nm, respectively, irrespective of the growth conditions. Raman analysis reveals that the synthesized graphene nano-flakes are of high quality since the $I_D/I_G$ ratio, a measure of quality of the material, is found to be less than 0.33 in spite of having contribution from edges of the nano-flakes to the D band emission intensity ($I_D$). Since the variation of $I_D/I_G$ ratio with growth conditions is insignificant, the observed variation of plasma or particle temperature with growth conditions is uncorrelated with the quality of the synthesized graphene nano-flakes.

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