

Research Paper

Effective Control of CH₄/H₂ Plasma Condition to Synthesize Graphene Nano-walls with Controlled Morphology and Structural Quality

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Abstract The direct growth method is simplified manufacturing process used to avoid damages and contaminants from the graphene transfer process. In this paper, graphene nano-walls (GNWs) were direct synthesized using electron cyclotron resonance (ECR) plasma by varying the CH₄/H₂ gas flow rate on the copper foil at low temperature (without substrate heater). Investigations were carried out of the changes in the morphology and characteristic of GNWs due to the relative intensity of hydrocarbon radical and molecule in the ECR plasma. The results of these investigations were then discussed.

Keywords: PECVD, Graphene nano-walls, Direct growth, Langmuir probe, Raman, RGA

I. Introduction

Graphene, a two-dimensional structure, has attracted considerable attention in an effort to explore its potential applications in various devices, including solar cells, supercapacitors, light-emitting diodes, touch-screen and sensors. The popularity of graphene is due to its excellent electronic property with an electron mobility of 200,000 cm²/Vs at room temperature, optical property with a transmittance of 97.7%, mechanical property with a Young's modulus of 1 TPa, and thermal property with a thermal conductivity of 5000 W/mK [1-6].

Graphene synthesizing methods for large area graphene films with high quality have been continuously developed [7-9]. Thermal chemical vapor deposition (CVD) is the most popular technique to overcome the limitations of scalability. However graphene synthesis using CVD techniques cannot change the morphology of the graphene surface because of the limitations intrinsic to the CVD method. On the other hand, the graphene synthesis method using plasma is more easily controlled due to the many process parameters affecting the growing morphology and structure of graphene [10,11]. In this paper, we studied the change of GNWs growth according to the relative ratio of hydrocarbon radical and molecule. we present a direct growth method of GNWs on Cu (100) foil substrates. The GNWs were directly grown on Cu foil by methane diluted

in hydrogen ECR plasma at low temperature. The density, temperature and potential of plasma were measured using a cylindrical Langmuire probe. We discussed the morphology and characteristic of the GNWs based on the results of field-emission scattering electron transmission (FE-SEM), residual gas analysis (RGA), Fourier-transform infrared spectroscopy (FT-IR), optical emission spectroscopy (OES) and Raman spectroscopy.

II. Experimental

1. Experimental conditions and sample preparations

The GNWs were deposited on Cu foil by ECR plasma system. A schematic illustration of the experimental equipment used in this study in Fig. 1. This system is composed of an electromagnet and a microwave system(without substrate heater). Microwave power is introduced to the plasma chamber through a bending waveguide and a window fabricated of a fused circular quartz. An electromagnet is arranged around the periphery of the circular quartz for ECR plasma excitation. The chamber was pumped to a base pressure of 10⁻⁶ Torr before synthesis and the input microwave power of 1.5 kW and process pressure of a few mTorr were introduced while GNWs synthesized. Cu foil with a thickness of 25 μm and area of 100 cm² was used as the experimental substrate (99.95%, Alfa Aesar). Table 1 shows the experimental conditions of the GNWs depositions with the gas flow rate and interaction times. The first step involved plasma cleaning and annealing of the substrate surface, while the

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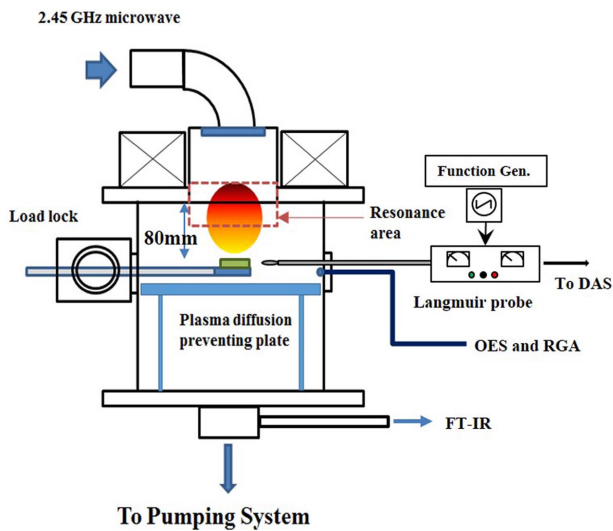


Figure 1. Schematic illustration of the experimental ECR plasma system.

Table 1. Conditions of GNWs for the gas flow rate on Cu foil.

Sample name	Flow rate [sccm]		Step 1: H ₂ plasma	Step 2: H ₂ +CH ₄ plasma
	H ₂	CH ₄	Interaction time [min]	
GNWs_20	200	20	3	5
GNWs_40	200	40	3	5
GNWs_120	200	120	3	5
GNWs_180	200	180	3	5

second step involved the deposition of the GNWs on the substrate. H₂ gas was used in the plasma cleaning and annealing of the Cu substrate. The second step of the GNWs deposition process was performed using the mixed gas plasma of CH₄ (carbon precursor gas) and H₂. The input microwave power to generate the plasma was 1.5 kW. The ECR discharge point was set at approximately 150 mm from the Cu substrate.

2. Measurements and analysis

FE-SEM (Gemini, Zeiss) was carried out to observe the surface morphology of the GNWs. The crystallinity and structural information of the synthesized GNWs were obtained by micro-Raman spectroscopy (in-Via Raman microscope, Renishaw) using a 532 nm laser. A minimal laser power of ~1 mW was used during the measurements to avoid damage of the GNWs. The optical emission spectroscopy (focal length : 750 mm, detector : CCD iDus 420, Andor) allows observations of only radicals where optical emission transitions are permitted by selection rules. On the other hand, optical emission transitions can be forbidden in many other radicals such as CH₃, CH₂, C₂H₂, etc. Therefore, other diagnostics such as FT-IR, RGA, ultraviolet absorption spectroscopy, etc. should be carried out to detect species that could also play an important role in the growth of GNWs [12]. An RGA (RGA100, Stanford Research System) is attached to the

side wall of the chamber to investigate the density of the synthesis radicals and molecules. FT-IR (Vertex 70, Bruker) spectrum was measured for hydrocarbon molecule intensity in the range of 500–4000 cm⁻¹. The density, temperature and potential of plasma were measured using the cylindrical Langmuire probe (handmade).

III. Results and Discussion

1. Synthesis and crystallinity properties of GNWs

The morphologies of the synthesized GNWs are shown in Fig. 2 at each conditions. When increasing the inlet CH₄ flow rate, the inter layer spacing and size of GNWs are further increased. The results show that the CH₄/H₂ ratio is an important factor in the synthesis of GNWs. Raman spectroscopy is an effective tool to evaluate nano-carbon materials. Fig. 3 shows the Raman spectrum of the GNWs on Cu foil by ECR plasma. Three peaks were observed at 1350, 1580, and 2700 cm⁻¹, corresponding to the D band, G band, and 2D band, respectively. The D band and the 2D band, generated by double resonant Raman scattering, can often be used to evaluate the grain size of graphene and the number of graphene layers. And intensity ratio of the D and G peaks, I_D/I_G indicates that size of crystalline grains as well as the inter defect distance [13,14]. The I_D/I_G ratio tend to increase as the inlet CH₄ flow rate increases. This result indicates the degradation of the quality of the GNWs. However, the I_{2D}/I_G ratio decreased as the inlet CH₄ flow rate increased. This implies an increase in the

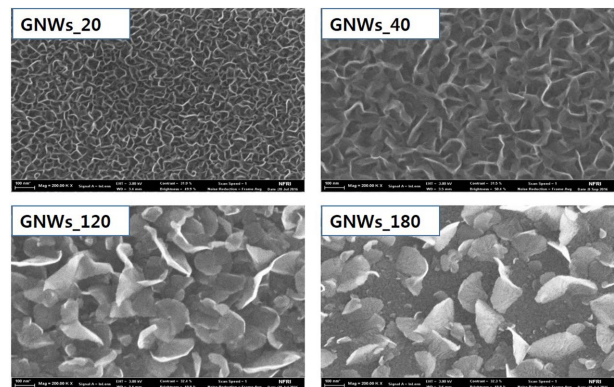


Figure 2. Plan view FE-SEM images of GNWs grown on Cu foil at 2–4 mTorr pressure with ECR plasma power of 1.5kW. Scale bars, 100 nm.

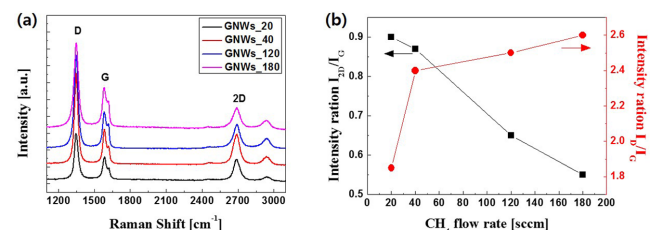


Figure 3. Comparison of Raman spectra at 514 nm for GNWs at each condition. (a) the intensities of the spectra are vertically offset for clarity (b) intensity ratio of D, 2D and G band.

graphene nano wall layer of the GNWs [15].

2. OES and RGA results during to synthesis GNWs

Fig. 4 show the OES results from the CH₄/H₂ plasma at each conditions. Optical emission lines derived from the CH (B²Σ-X²Π and A²Δ-X²Π), H_γ (434 nm) and C₂ swan system (approximately 516.5 nm) were principally observed. The detection of CH, the C₂ species, and the atomic and molecular hydrogen imply an effective dissociation of the C source molecules by the ECR plasma. Fig. 4(b) shows the increase in the CH radical emission intensity as the inlet CH₄ flow rate increases. We calculated the CH radical rotational temperature using the results shown in Fig. 4(b) and identified the correlation between the calculation and synthesis of the GNWs [16]. However, it is difficult to calculate the current measurement system because of its low resolution. Therefore, we performed additional experiments

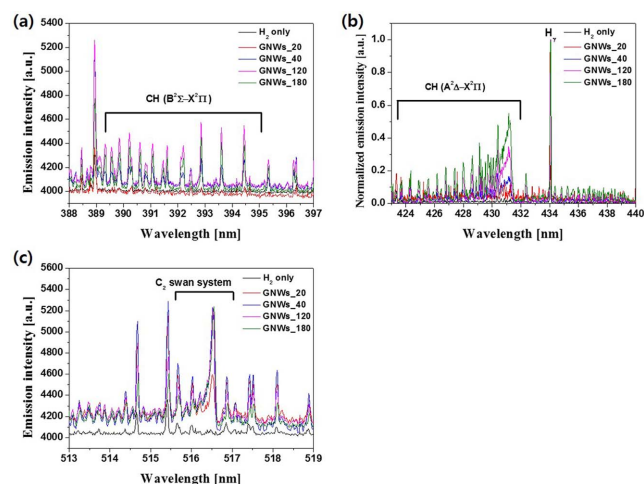


Figure 4. Typical optical emission spectra from CH₄/H₂ plasma at each condition. (a) CH (B²Σ-X²Π) system, (b) measured CH (A²Δ-X²Π) system and H_γ emission intensity normalized by H_γ peak intensity (at 434 nm), and (c) C₂ swan system emission results.

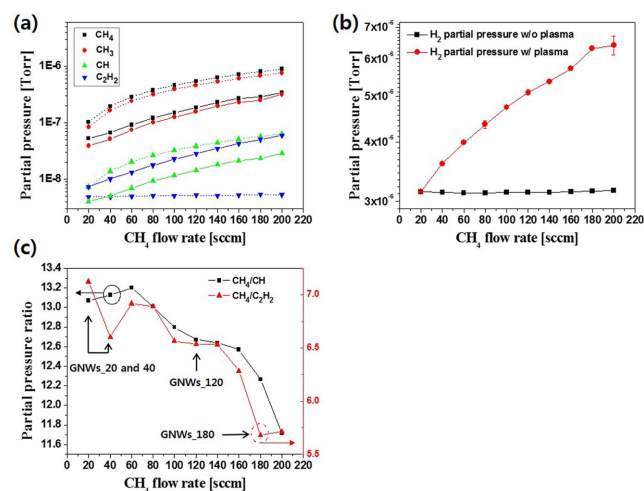


Figure 5. Partial pressure(or partial pressure ratio) variations of (a) hydrocarbon radical and molecule, (b) H₂, and (c) CH₄/CH and CH₄/C₂H₂ as functions of CH₄ flow rate measured by RGA.

after the equipment improvement. As explained above, the optical emission transitions might be forbidden in many other radicals such as CH₃, CH₂, C₂H₂, etc. Therefore, hydrocarbon radicals and molecules were measured using RGA.

CH₄ provides hydrogen species during its dissociation process into active species. In thermal CVD, only ~0.0002% of incoming methane dissociates from the active species in the gas phase at a temperature of 900°C. However, more than 80% of methane dissociates from other species such as H, H₂, CH, C₂H₂, etc. due to the advantage of plasma [17]. The measured RGA results are shown in Fig. 5. Fig. 5(a) shows the partial pressure of hydrocarbon molecules and radicals. The solid line represents the measured results of the ECR plasma generation and the dotted line represents the measured results of the pre-plasma generation. The partial pressure of CH₄, CH₃ and CH was relatively reduced compared to the pre-plasma generation, while the partial pressure of C₂H₂ increased during plasma generation. Fig. 5(b) shows the variation of partial pressure of H₂ as a function of the CH₄ flow rate. The hydrogen partial pressure was increased with increasing CH₄ methane flow rate during the plasma generation. The increase of the inter layer spacing of the GNWs shown in Fig. 2 is due to an increase in the hydrogen partial pressure. This is because hydrogen, hydrogen atoms, and radicals attack the carbon atoms at surface defects via C-H covalent bond formation and C-C bond breakage [18]. Fig. 5(c) shows the partial pressure ratio of CH₄/CH and CH₄/C₂H₂, and the experiments condition GNWs₂₀, GNWs₄₀, GNWs₁₂₀, and GNWs₁₈₀. When the CH₄ flow rate was increasing, the partial pressure of CH and C₂H₂ increased compared to CH₄. The growth of the GNWs requires more atomic carbon from the process of the hydrocarbon radicals and molecules via H-bond breaking and H₂ molecule formation, respectively. C₂H₂ had a higher dehydrogenation energy (879 kJ/mole) than other hydrocarbon molecules and radicals. In the case of C₂H₂, difficulties arose in making atomic carbon because of the carbon triple bond.

3. Langmuir probe analysis and FT-IR measured results during to synthesis GNWs

Fig. 6 shows the FT-IR absorption spectra of the exhaust gas during the process of the synthesis the GNWs. CH₄ was identified from the peak in the wave number range of 1220-1380; 2850-3150 cm⁻¹. It should be noted that the diatomic molecules such as H₂ could not be identified by FT-IR. As the flow rate of CH₄ increased, the increase of C₂H₂ and Alkyne intensity was observed. In the case of C₂H₂ and Alkyne, these compounds are of carbon triple bonds and have a high binding energy, so it is difficult to generate carbon atoms by breaking bonds. Therefore, the increase of the applied CH₄ flow rate increased the ratio of the carbon triple bond, it is thus difficult to growth GNWs

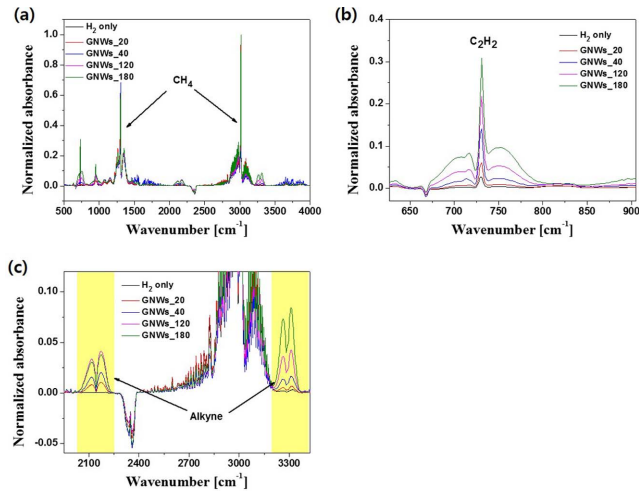


Figure 6. (a) Measured FT-IR absorption spectra normalized by CH₄ main peak intensity (approximately 3018/cm) variations as function of CH₄ flow rate (b) C₂H₂ and (c) alkyne identified by the peak in the wave number range of 650-800/cm and 2050-2200;3200-3400/cm, respectively.

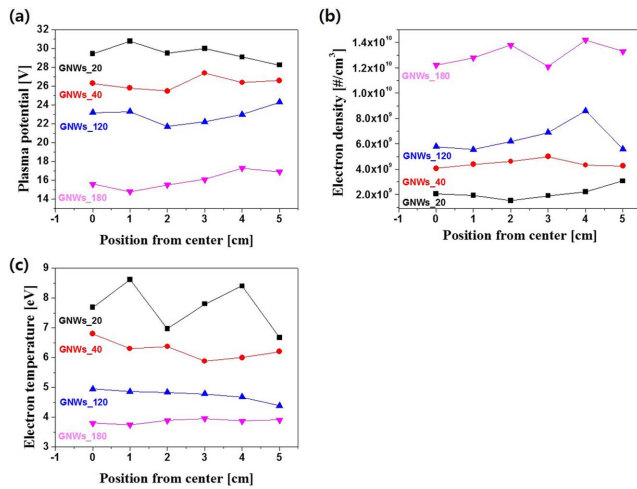


Figure 7. (a) Plasma potential, (b) electron density, and (c) electron temperature of the ECR plasma equipment at each condition.

due to the difficulty in producing carbon atoms as a source of the synthesis of GNWs. The increasing C₂H₂ intensity is due to the inelastic collisions of methane molecules with free electrons (generated by ECR plasma), leading to the formation of some active radicals such as CH₃, CH₂, CH and C₂H. The formation of gaseous C₂H₂ can be attributed to the following two possible channels [19]:

- 1) Recombination of radicals: $\text{CH} + \text{CH} \rightarrow \text{C}_2\text{H}_2$; $\text{H} + \text{C}_2\text{H} \rightarrow \text{C}_2\text{H}_2$, etc.
- 2) Inelastic collisions of methane molecules with radicals: $\text{C} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$, etc.

Ethane C₂H₆ has been widely reported as an important gaseous hydrocarbons in dielectric-barrier discharge (DBD) and pulsed glow plasma because of the recombination of high concentration CH₃ radicals [20,21]. However, no obvious C₂H₆ was detected in the current work. This is possibly because the electron temperature

from the ECR plasma is a greater than that of the DBD and glow plasma. Therefore, an enhanced dehydrogenation process of C₂H₆ is induced by the impact of electrons or radical collisions. Plasma physicists use Langmuir probes in low temperature plasmas to measure the electron density, electron temperature and plasma potential. A Langmuir probe was located 10 mm above the substrate and was used to measure the parameters in the radial direction at 10 mm intervals. The Laframboise plot is used to determine the plasma parameters [22]. The measured plasma temperature, density and potential are shown in Fig. 7.

The measured plasma potential of each experimental conditions is shown in Fig. 7(a). It can be confirmed that the plasma potential decreased as the applied CH₄ gas flow rate increases. The intensity of the plasma potential is proportional to the intensity of the electric field formed perpendicularly to the Cu foil surface. Therefore, it can be confirmed, as shown in Fig. 2, that the intensity of the electric field on the surface of the Cu foil decreased and the GNWs are not synthesized vertically with the increase of the applied methane gas flow rate increase [23]. The bulk of the plasma is ion and electron densities are nearly equal, $n_i \approx n_e$, a condition commonly known as “quasi-neutral”. Fig. 7(b) shows that the electron density increased as the CH₄ gas flow rate was increased because the pressure inside the chamber increases. On the other hand, Fig. 7(c) shows the reduction of electron temperature due to the reduced mean free path of electrons. 1 eV is approximately 11600 K. The reduction of the electron temperature affects the surface temperature change of the Cu foil as well as the growth of GNWs. CH₄ undergoes a dehydrogenation process to produce four H atoms and a C atom needed for the growth of the GNWs. The relative dehydrogenation energy of the CH₄ on the Cu surface increases as the dehydrogenation process progresses [24]. Therefore, if the electron temperature is low, the supply of carbon necessary for the growth of GNWs cannot proceed smoothly.

IV. Conclusions

We have investigated the properties of GNWs synthesized using ECR plasma and the ECR plasmas' characteristics was diagnosed. As the flow rate of CH₄ is increased, the partial pressure of hydrogen increases, which etches the carbon onto the surface of the GNWs, destroying the C-C bond and increasing the C-H covalent bond, and increase the number of carbon triple bond molecules. This is considered an unfavorable environment for GNWs growth. However, the increase of the relative partial pressure of the CH radical due to the increase of the applied CH₄ flow rate is considered to be the cause of the carbon supply for the GNWs growth because the binding energy of the CH radical is as low as 3.72 eV. Therefore, the appropriate hydrocarbon radical and molecular ratios,

and the hydrogen partial pressure are considered necessary. The electron temperature and plasma potential decreased with the increasing CH₄ flow rate. The changes in the electron temperature and plasma potential affect to changes in the temperature and electric field on the surface of the Cu foil, influencing GNWs growth. Plasma diagnostics should thus be performed in GNWs synthesis research in which plasma is used.

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