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Research Article

Spectral Monitoring CH/C_2 Ratio of Methane Plasma for Growing Single-Layer Graphene on Cu

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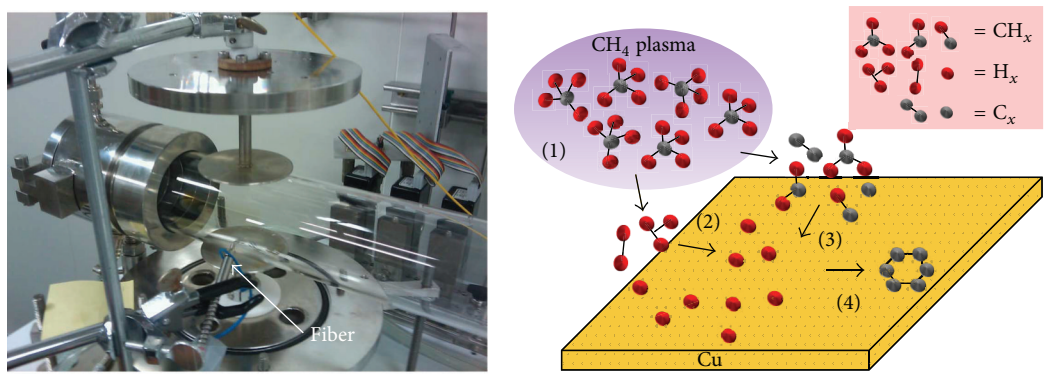
Single-layer graphene was grown on copper at a low temperature of 600°C by plasma-assisted thermal chemical vapor deposition. Its growth mechanism was discussed with reference to the emission spectra of the plasma. The methane plasma produces the active species (H_x, CH_x, and C_x) without the addition of flowing hydrogen, and the amounts of hydrogen-containing species can be controlled by varying the plasma power. The effective distance was found between the plasma initial stage and the deposition stage for the single-layer graphene synthesis. The results reveal that high-quality graphene can be synthesized using methane plasma at a suitable plasma power.

1. Introduction

Graphene is a flat monolayer of carbon atoms that are tightly packed into a two-dimensional honeycomb lattice. It is a basic constituent of graphitic materials, such as 0D fullerenes, 1D carbon nanotubes, and 3D graphite [1]. The physical properties of graphene favor a wide range of applications [2–4]. The mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) yields grains of high-quality graphene with dimensions of the order of micrometers [5]. However, this method cannot provide large quantities of graphene sheets, which are required for several purposes. Chemical exfoliation is a promising means of obtaining high-throughput graphene sheets from bulk graphite [6]. This method uses acid solution as an oxidizing agent to form graphene oxide, which is subsequently reduced to graphene, but the graphene thus formed has various defects, which worsen its physical properties. Another method is the thermal decomposition of SiC substrate, in which Si atoms on the surface of the substrate are exposed to a temperature of 1050°C to 1100°C [7], but the effective area of graphene on the SiC is difficult to control, and the use of an expensive one is not practical. Li et al. were recently the first authors to demonstrate the use of chemical vapor deposition (CVD) to grow single-layer graphene on copper from a mixture of hydrogen and methane gases in a vacuum [8]. Carbon is only weakly soluble in Cu, allowing the formation of single-layer graphene by self-limiting growth [9]. The quality of CVD-grown graphene depends on the growth conditions, and the growth mechanism has been investigated elsewhere [10, 11]. Vlassiouk et al. showed that hydrogen plays an important role in control of the morphology, domains, and layers of CVD-graphene and acts as a catalyst in graphene synthesis [10]. The synthesis temperature of CVD-graphene is as high as 1000°C, limiting its range of applications. Therefore, a low-temperature synthetic process for graphene must be developed. The plasma CVD method enables graphene to be grown at a lower temperature. Terasawa and Saiki studied the use of a plasma-enhanced CVD (PE-CVD) system for synthesizing graphene at a low temperature of 500°C [12]. Surface wave plasma CVD (SWP-CVD) has been utilized to synthesize graphene electrodes at a low temperature of around 300°C [13]. However, these methods require expensive equipment and the ion bombardment effect produces various defects. To clarify the mechanism of growth of graphene in a plasma system, the atomic and molecular lines in the spectra of



(a) (b)

FIGURE 1: (a) Plasma-assisted CVD system apparatus that is composed of two parallel negative and positive electrodes, and the optical fiber was used to obtain the plasma emission spectra. (b) Transport kinetics of gaseous species that are formed by decomposition from methane and used in graphene growth include four steps.

ionized methane/hydrogen mixture gas are identified [14]. Hydrocarbon gases are the most commonly chosen carbon source for synthesizing graphene; these include methane (CH_4) and acetylene (C_2H_2) [15, 16]. Hydrogen can be formed by the decomposition of hydrocarbon in a cocatalyst reaction that also provides active carbon species (CH_x and C_x) [10], which react to form graphene. To this end, graphene films are grown herein without hydrogen by exploiting the dissociation of hydrocarbon at low temperature by plasma-assisted thermal CVD. The plasma emission spectra were obtained during plasma-assisted thermal CVD to elucidate the mechanism of growth of graphene.

2. Experiment

Throughout the experiments, plasma-assisted thermal CVD was carried out to synthesize graphene films on polycrystalline copper foil with various plasma powers from 110 to 200 W at a temperature as low as 600°C. Figure 1(a) presents an apparatus that is composed of two parallel negative and positive electrodes and a direct current (DC) pulsed power supply that generated the plasma. The voltage and current were around 600 V and 330 mA, respectively. The DC pulse frequency was 1 kHz. Optical fiber was mounted next to the furnace to obtain the plasma emission spectra. Raman spectroscopy yielded the entropy of graphene films to which an excitation laser beam with a wavelength of 532 nm and a power of 1.2 mW focused at a spot was applied.

To grow CVD-graphene on copper, 25 μm thick polycrystalline copper foil (99.8%, Alfa Aesar, item number 13382, Ward Hill, MA, USA) was placed on a quartz plate and then loaded into the center of the tube furnace. The effective distance between the plasma and the center of the hot zone was varied from 30 to 90 cm to grow graphene. Prior to growth, the copper foil was electropolished in an ice bath that contained 100 mL of phosphoric acid and 50 mL of deionized water, before being biased at 3 V for 60 s; it was then rinsed in deionized water with sonication and dried in an atmosphere of nitrogen for 5 min. The furnace was pumped down to a base pressure of 3×10^{-3} Torr and the temperature was ramped up to 1035°C with a constant 2 sccm flow of hydrogen plasma. Then, the Cu foil was annealed for 30 min at a temperature of 1035°C. During the growth step, the temperature was reduced to 600°C, and the plasma was then used to dissociate the methane gas that was flowing over it at a rate of 30 sccm to generate hydrogen (H_x) and the active carbon species (C_x, CH_x), under a pressure that was controlled at 1.8×10^{-1} Torr for 10 min to enable the graphene to grow. The graphene films grew on copper with plasma powers of 0 W, 110 W, 140 W, 170 W, and 200 W. The sample was then cooled down by removing it from the hot zone of the furnace to complete the growth step. The as-grown graphene films were transferred onto SiO_2 (300 nm)/Si substrates by etching away the copper foil in an iron chloride ($FeCl_3$) solution. Before wet etching, a 200 nm thick PMMA (poly-methyl-methacrylate) layer was spin-coated on the top of graphene/copper foil, which was then baked at 130°C for 1 min. The PMMA-caped graphene film was floated on the solution surface before being washed in dilute hydrochloric acid to remove the etchant and metal ions; it was then rinsed in deionized water. PMMA/graphene films were placed on the SiO_2 (300 nm)/Si substrate and then dried on a hot plate at 70°C for 10 min; the PMMA was then dissolved in an acetone bath over 24 h.

Figure 1(b) plots the transport kinetics of gas species that were formed by the decomposition of methane and used to grow graphene. The procedure is proposed to have the following four steps. (1) Methane plasma generates hydrogen-containing species as it decomposes into hydrogen and active species. The active species are H_x, C_x, and CH_x radicals. (2) H_x species were absorbed on the copper as a cocatalytic reactor. (3) Various CH_x radicals were chemisorbed by the copper surface and decomposed to generate carbon species. (4) Active carbon species formed a sp^2 crystal lattice; the gaseous by-products of the reaction were desorbed from the copper surface and diffused away. As already mentioned, in

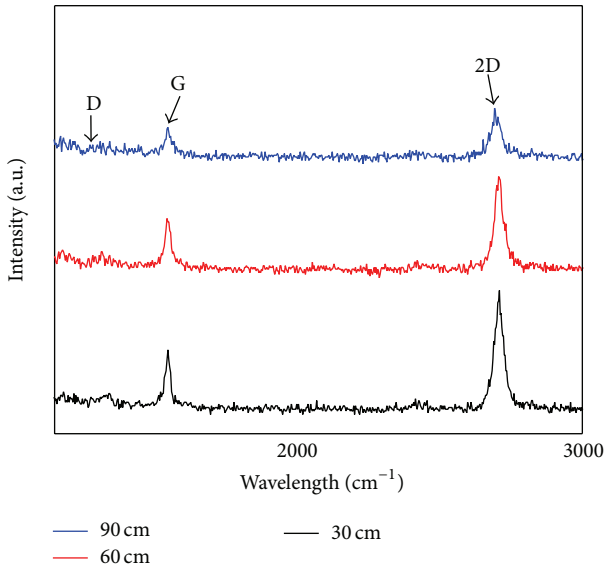


FIGURE 2: Raman spectra of graphene films synthesized with distances from 30 to 90 cm between initial stage of plasma and sample, with a plasma power of 200 W.

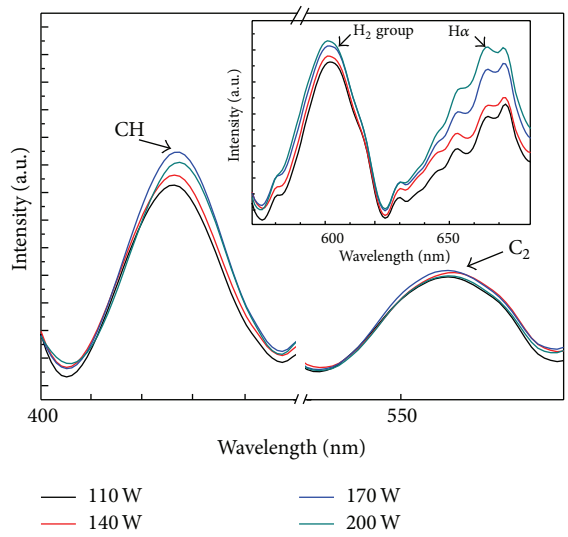


FIGURE 3: Typical plasma emission spectra of methane obtained with various plasma powers from 110 W to 200 W.

kinetic model of graphene growth by plasma-assisted CVD, the distance between the plasma and the center of the hot zone affects the total growth.

3. Results and Discussion

Figure 2 displays the Raman spectra of graphene films that were grown on copper using a constant DC-pulsed power of 200W, with various distances of 30 to 90 cm between plasma and the growth sample. The Lorentzian 2D band increased as the distance decreased because the rate of recombination decreased. In this case, the effective distance was an important factor in promoting the growth of graphene in the plasma system. Figure 3 shows plasma emission spectra of methane gas obtained with various plasma powers. Following ionization, the excited electrons recombined with protons to form new atoms and molecules. The H_x spectra and the CH_x spectra were obtained after these species had moved by certain distance [17]. The transition from $n = 3$ to $n = 2$ is called H-alpha (H_α) and emitsa wavelength of approximately 656 nm. Another recombination line of molecular hydrogen (H_2) dominates the emission spectra at wavelengths of 550 to 650 nm. The emission spectra peaks of CH radicals (430 nm) and C_2 (541 nm) were also obtained [14]. H_α is formed when hydrogen is ionized, and the peak intensity increases with the DC power. Interestingly, the intensity of the CH spectral peak that was obtained at a DC power of 170 W exceeded that obtained at a DC power of 200 W. Hydrogen is strongly well known to affect the activation of CH_x radicals into more active species. The dissociation of ionized hydrogens proceeded to saturation herein, limiting the CH_x recombination. Additionally, the C_2 dimers are critical to the formation of various carbon materials during the plasma system [18], generating a carbine structure to yield a two-dimensional

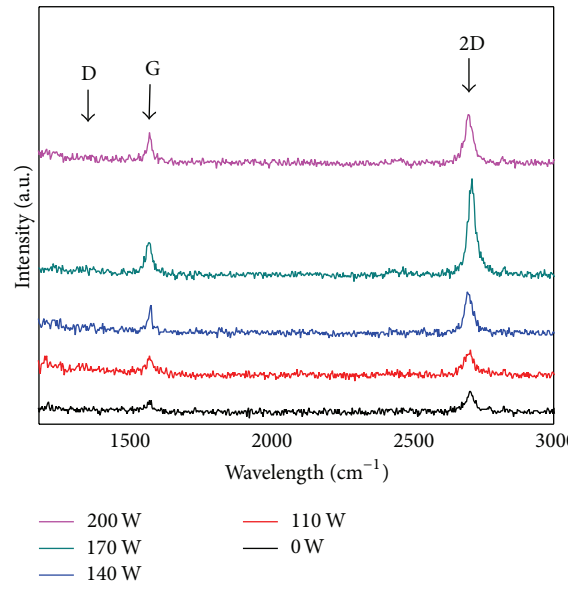


FIGURE 4: Raman spectra of graphene films synthesized with various plasma powers from 0 W to 200 W and an effective distanceof 30 cm.

carbon material, graphene. Since the formation of graphene by plasma-assisted thermal CVD with an effective distance of 30 cm was verified, the Raman spectra of graphene that was synthesized at various powers were obtained and shown in Figure 4.

The Raman spectra include common peaks of D, G, and 2D at around 1360, 1560, and 2700 cm^{-1}, respectively [19]. The D peak is associated with the breathing modes of sp^2 atoms, which are induced by defects in the disorder at the edge of the graphene in the sample [20, 21]. The G peak is associated with the doubly degenerate phonon mode at the center of the Brillouin zone and reveals the sp^2 carbon structure [22]. However, the most well-known feature in

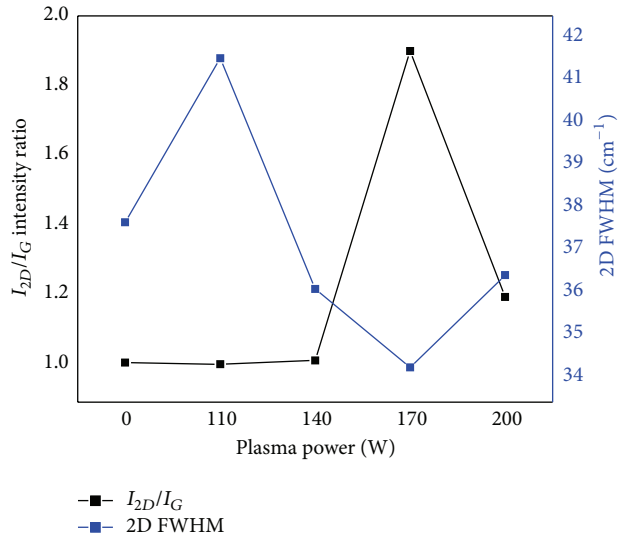


Figure 5: FWHM of 2D peak and ratio of intensity of 2D to that of G peak as functions of plasma power.

the spectrum of graphene is the 2D peak, which is always seen even when no D peak is present [23]. Details of the Raman features of graphene are discussed elsewhere [19, 23]. The samples that were synthesized at low temperature do not yield the D peak, indicating that these graphene films were synthesized without defects in the system herein. The intensity of 2D peak increased with the plasma power from 0 W to 170 W because of the cocatalytic activity of hydrogen that was formed by the decomposition of methane plasma, which increased the size of the grains of the synthesized graphene and prevented disorder in its growth. A plasma power of over 170 W provided more hydrogen for etching, reducing the size of the graphene grains and the intensity of the 2D peak [24]. This result is consistent with Figure 3.

Figure 5 displays the ratio of the intensity of the 2D peak to that of the G peak (I_{2D}/I_G), 1.9, and the full width at half maximum (FWHM) of the 2D peak, 34.5 cm^{-1}, at a plasma power of 170 W. A higher plasma power promotes the decomposition of methane and better ensures the sufficiency of hydrogen species for synthesizing high-quality graphene. Interestingly, the ratio I_{2D}/I_G decreased and the FWHM of the 2D band increased with increasing plasma power up to 200 W, indicating that the grains became smaller, owing to the hydrogen etching effect.

4. Conclusion

In summary, single-layer graphene was grown on copper at low temperature by plasma-assisted thermal CVD. The optimal distance tested herein was 30 cm between the initial stage of the plasma and the sample affecting the recombination rate in the single-layer graphene synthesis. The ratio I_{2D}/I_G and the FWHM of the 2D peak were 1.9 and 34.5 cm^{-1} at plasma power of 170 W. The amount of generated hydrogen species can be controlled by varying the plasma power and reached saturation when the plasma power exceeded 170 W. This work demonstrates plasma-assisted thermal CVD for synthesizing single-layer graphene and clarifies the mechanism of graphene growth by directly observing the plasma emission spectrum following the decomposition of methane.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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