Fabrication of graphene-based materials
using microwave-exited non-equilibrium atmospheric pressure plasma

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Abstract: A non-equilibrium atmospheric pressure plasma-enhanced chemical vapor deposition (PECVD) employing He/H$_2$/CH$_4$ mixture is applied to the synthesis of several carbon nanostructures. Few-layer graphene films can be formed on the Cu substrate, indicating that the self-limited growth can be attained using the high-pressure radical source. Carbon nanowalls (CNWs) were synthesized on a Si substrate with Ti nanoparticles. In addition, aligned carbon nanotube (CNT) films were synthesized on a Co-catalyzed Si substrate with TiN buffer layer.

Keywords: graphene-based materials, nano-carbon, atmospheric pressure plasma

1. Introduction

Graphene-based materials such as carbon nanotube (CNT) and graphene itself have attracted much attention due to their emerging applications. Graphene-based materials can be synthesized by several plasma enhanced chemical vapor deposition (PECVD) techniques on heated substrates employing CH$_4$ and H$_2$ mixtures. For example, plane graphene can be formed by PECVD on Cu and Ni in the remote plasma configuration. However, excess flux of carbon precursors causes supersaturation and ion bombardment induces the nucleation of nanographene, resulting in the formation of vertical nanographene (carbon nanowall, CNW). CNTs can be grown on the metal-catalyzed Si substrate in the presence of buffer layer such as Al and Ti to prevent the formation of metal silicide. In other words, the structure of graphene-based architecture highly depends on the nucleation even under the same condition of plasma used for the growth.

A microwave-excited non-epuilibrium atmospheric pressure plasma source with high electron density of ~10^{15} cm^{-3} and low electron temperature of ~1 eV was applied to the synthesis of CNT films [1]. This type of plasma has a great potential for realizing the new material processing because the larger amount of radicals is estimated by a few orders of magnitude compared with the conventional low-pressure and high-density plasmas. On the other hand, the effect of ion bombardment on the growing surface can be removed due to the high-pressure operation. Therefore, special treatment of substrate or selection of substrate should be considered for the nucleation of graphene-based materials with various structures.

In this work, microwave-excited atmospheric pressure plasma was applied to the synthesis of graphene-based materials including few-layer graphene parallel to the substrate, CNWs as well as aligned CNTs, by the selection of substrate or controlling the surface treatment of Si substrate using metal nanoparticles.

2. Experimental

A schematic of non-equilibrium atmospheric pressure plasma-enhanced CVD system is shown in Fig. 1. The microwave (2.45 GHz) propagates from the top of the deposition chamber to the micro-slit electrode. The micro-slit electrode width is 0.2 mm and the distance between substrate and the micro-slit is 5 mm. A source gas mixture (He/H$_2$/CH$_4$) is introduced from the upper part of the micro-gap and pumped out from the lower part of the deposition chamber, such that the chamber pressure is kept at atmospheric pressure.

Formation of plane graphene was carried out on Cu substrate for 10-300 sec at a microwave power of 100 W, a total pressure of 1 atm and a substrate temperature of about 700 ˚C. The flow rates of He, CH$_4$ and H$_2$ were 5000, 20 and 50 sccm, respectively.

In the case of CNW fabrication, growth experiments were carried out for 30 min at a microwave power of 300 W. Prior to the CNW growth, Ti nanoparticles were formed on the Si substrate using pulsed arc plasma deposition. The flow rates of He, CH$_4$ and H$_2$ were 1000, 25 and 25 sccm, respectively.

CNT growth was carried out for 5 min at a microwave power of 100 W. Prior to the CNT growth, catalytic Co nanoparticles were formed on the TiN-coated Si substrate using pulsed arc plasma deposition.
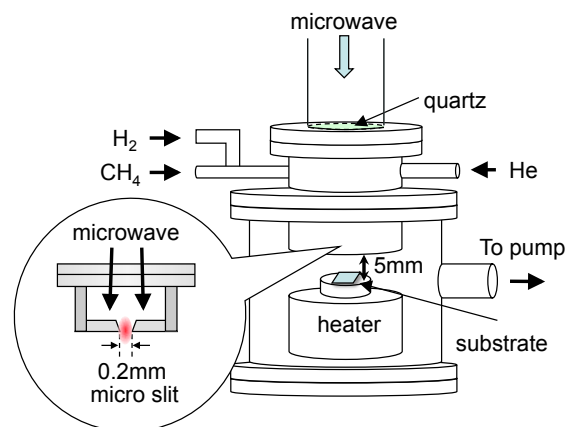

Fig. 1. Schematic of atmospheric pressure plasma enhanced CVD system.

3. Results and Discussion

Figure 2(a) shows Raman spectra of graphene-based films formed for 120 sec on Cu substrate at various distance from plasma. [A] - [F] in Fig. 2(a) correspond to the positions shown in Fig. 2(b). Position B is directly below the slit-shaped plasma. The Raman spectra of the film show three peaks centered at 1350, 1580, and 2690 cm^{-1}, which are assigned to the D, G, and 2D bands, respectively. The strong G band peak indicates the formation of a graphitized structure. The D band peak corresponds to the disorder-induced phonon mode, which is attributed to the defects or structural disorder in graphenes. The prominent feature in the Raman spectra of graphene is the 2D band peak. The 2D band peak is used to confirm the presence of graphene, and it originates from a double resonance process that links phonons to the electronic band structure. The intensity ratio of the 2D to G band peaks has a good correlation with the number of graphene layers [2,3]. The intensity ratio of the 2D band peak to the G band peak (I_{2D}/I_G) in the Raman spectra of graphene increases with decreasing number of graphene layers. In the Raman spectra shown in Fig. 2(a), the existence of D band peak suggests a nanocrystalline structure and the presence of domain boundaries, due to the rough surface of Cu substrate. On the other hand, the I_{2D}/I_G ratios of Raman spectra at various positions are almost same value (~0.5). It is noted that the G/D and G/2D ratios did not depend on the distance from the slit-shaped plasma.
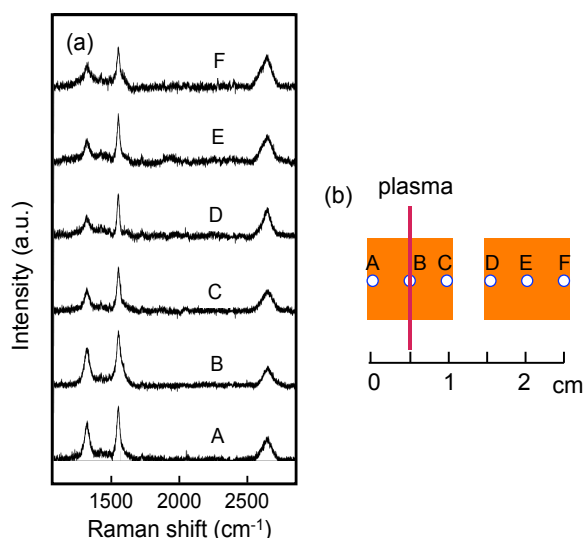

Fig. 2. (a) Raman spectra of graphene-based films formed for 120 sec on Cu substrate at various distances from plasma. (b) Schematic illustration showing the positions [A] to [F] relative to the slit-shaped plasma.

Figure 3 shows Raman spectra of graphene-based films formed on Cu substrate at position A for 30 and 300 sec. The Raman spectrum of graphene-based film formed for 300 sec was almost identical to that of the film formed for 30 sec, indicating that the number of graphene layers did not increase in spite of the increase of formation period. Results in Figs. 2 and 3 suggest that the self-limited growth of few-layer graphene can be attained on the Cu substrate using atmospheric pressure plasma. Film quality of graphene-based films could be improved by using highly crystalline Cu foil with minimum surface roughness as a substrate.
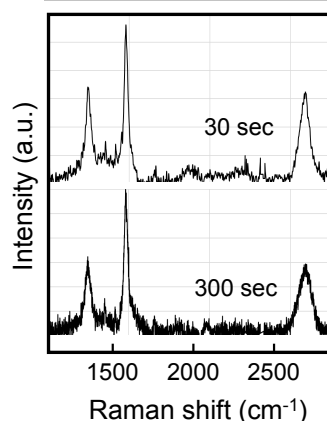

Fig. 3. Raman spectra of graphene-based films formed on Cu substrate at position A for 30 and 300 sec.

For the growth of CNWs on the Si or SiO$_2$ substrate, ion bombardment with appropriate energy and flux is necessary for the nucleation of vertical nanographene [4]. In the case using atmospheric pressure plasma, CNWs were not formed without ion bombardment due to the high-pressure operation. However, it was reported that the presence of Ti nanoparticles enhanced the nucleation of nanographenes [5]. Figure 4 shows SEM image of CNW film grown on the Ti-coated Si substrate by non-equilibrium atmospheric pressure plasma-enhanced CVD system employing CH$_4$/H$_2$/He mixture for 30 min. This image shows that two-dimensional carbon sheets were grown vertically on the substrate, forming a unique nanostructure similar to a maze. Height of the CNW film grown for 30 min was about 70 nm.
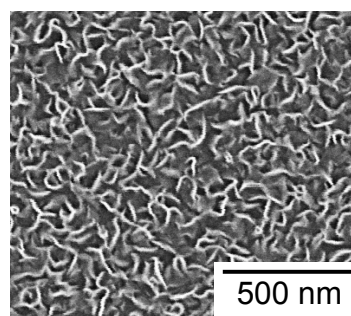

Fig. 4. SEM image of CNW film fabricated by non-equilibrium atmospheric pressure plasma-enhanced CVD system employing CH$_4$/H$_2$/He mixture for 30 min on the Ti-coated Si substrate.

Figures 5(a) and 5(b) show SEM image of aligned CNT film and TEM image of CNT, respectively, grown by non-equilibrium atmospheric pressure plasma-enhanced CVD. Vertically aligned CNT films were successfully synthesized using atmospheric pressure PECVD on the Co-catalyzed Si substrate. The pulsed arc plasma deposition with Co electrode yields Co nanoparticles of about 1–2 nm in size. In our system, it takes about 15 min to increase the heater temperature from room temperature to 700 ˚C. During this period, overlapped or closely adjacent particles can merge, resulting in the formation of catalytic nanoparticles of approximately 5–10 nm in size. The size of catalytic nanoparticles corresponds to the diameters of the grown CNTs. Growth rate of CNT film was about 130 nm/s.
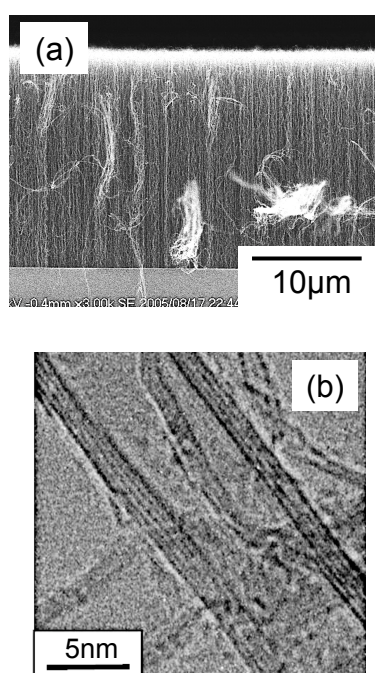

Fig. 5. (a) SEM image of aligned CNT film fabricated by non-equilibrium atmospheric pressure plasma-enhanced CVD employing $CH_4/H_2/He$ mixture for 5 min on the Co-catalyzed Si substrate. (b) TEM image of CNT fabricated by non-equilibrium atmospheric pressure plasma-enhanced CVD.

4. Summary

A microwave-excited non-epuilibrium atmospheric pressure plasma source employing $He/H_2/CH_4$ mixture was applied to the synthesis of graphene-based materials with different structures by the nucleation control. Few-layer graphene films can be formed on the Cu substrate. Results indicated that the self-limited growth of few-layer graphene could be attained on the Cu substrate by the supply of long-lived hydrocarbon radicals without ion bombardment using atmospheric pressure plasma. CNWs were synthesized on a Si substrate with Ti buffer layer. Aligned CNTs were also successfully synthesized on a Co-catalyzed Si substrate with TiN buffer layer. Results obtained in this work exhibit the effectiveness of microwave-excited non-epuilibrium atmospheric pressure plasma for the fabrication of carbon nanostructures.

5. References

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