Continuous Synthesis of Carbon Nanoparticles using Ar+CH_4 Multi-hollow Discharge Plasma CVD

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Abstract: We have succeeded in continuous synthesis of carbon nanoparticles (CNPs) using a multi-hollow discharge plasma chemical vapour deposition (CVD) reactor with Ar and CH_4 gas mixtures. We examined effects of gas mixture ratio of Ar and CH_4 on the CNPs synthesis. From TEM images, nanoparticles were observed for Ar:$CH_4 \geq$ 6:1. The size distribution of CNPs ranges from 5 to 80 nm. With increasing the Ar concentration, their size decreases while their density increases. Raman measurements show the nanoparticles have polymer-like structures.

Keywords: plasma chemical vapour deposition, carbon nanoparticle

1. Introduction

Along with the development of nanotechnology, interest in carbon nanomaterials has escalated and their application fields are diversifying. In particular, carbon nanoparticles (CNPs) have been studied in a wide range of fields due to their extensive characteristics such as mechanical, chemical properties and other attributes [1-3]. Among many methods to synthesize carbon nanoparticles, plasma process is one of the promising alternatives [4]. Various research groups have produced carbon nanomaterials using plasma, but applying them to diverse industrial fields requires a simple yet continuous and uniform deposition of nanomaterials. So far, we have successfully produced Si nanoparticles using a multi-hollow discharge plasma chemical vapour deposition (MHDPCVD) reactor with silane gas [5-7].

Here, we employed the MHDPCVD reactor to synthesize CNPs using Ar diluted CH_4 gas. We carried out continuous deposition of CNPs on a substrate aiming at their practical applications in the future. Then, we examined characteristics of CNPs as a parameter of the gas mixture ratio of Ar and CH_4.

2. Experimental

Figure 1 illustrates the schematic diagram of MHDPCVD reactor. First, the grounded and powered electrodes were set up in the chamber. These electrodes had 8 holes of 0.5 cm in diameter and 0.5 cm in length. Then, a mixed gas of Ar and CH_4 was supplied to the reactor with the total gas flow rate of 100 sccm. Total pressure was maintained at 2 Torr. 60 MHz radio frequency power of 40 W was applied to the electrodes through the matching box. Plasmas were generated in the holes of the electrodes. The experiments were carried out at room temperature (293K). The substrate holder was installed, grounded at 10 cm away from the electrodes in the downstream region. In addition, the substrate temperature was room one. Nanoparticles generated in the electrodes ultimately were transported to the substrate via gas viscous force [8].

To examine the produced CNPs, the nanoparticles were deposited on a high resolution TEM-grid and a N-type (100) Si substrate that were installed on the substrate holder. Moreover, A transmission electron microscope (JEOL, JEM-2010) was used to analyse the size distribution. Raman spectroscopy (Jasco, NRS-3000, excitation laser: 532 nm) was applied to analyse the structure of CNPs [9-11].

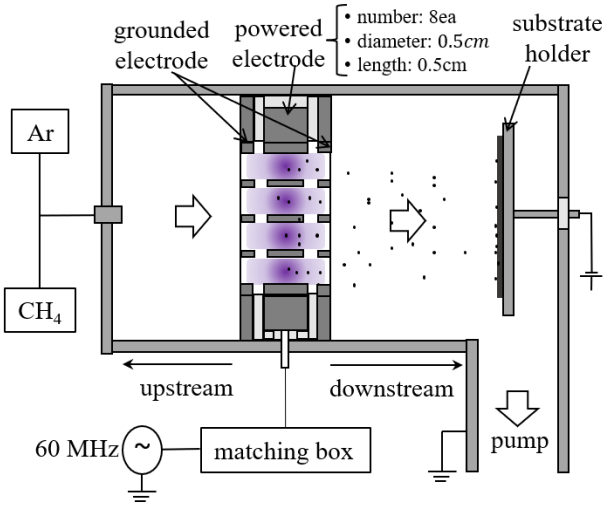

Fig. 1. Schematic diagram of MHDPCVD reactor.

3. Results and discussion

(1) Continuous synthesis of CNPs

Figure 2 displays the TEM images of the nanoparticles synthesized as a parameter of the ratio of Ar to CH_4. For the ratio of Ar to CH_4 of 1:1 (a) and 3:1 (b), no nanoparticle was observed on the TEM grids; whereas for 6:1 (c) to 9:1 (e), nanoparticles were densely deposited on the TEM grids. Figure 2(c-2) represents electron diffraction pattern of the deposited nanoparticles for 6:1. Since the diffraction pattern consists of a series of concentric diffuse rings rather than spots/ sharp rings, the CNPs have an amorphous structure.

Figure 3 depicts the surface density per unit area of nanoparticles deposited on TEM grids. The number and

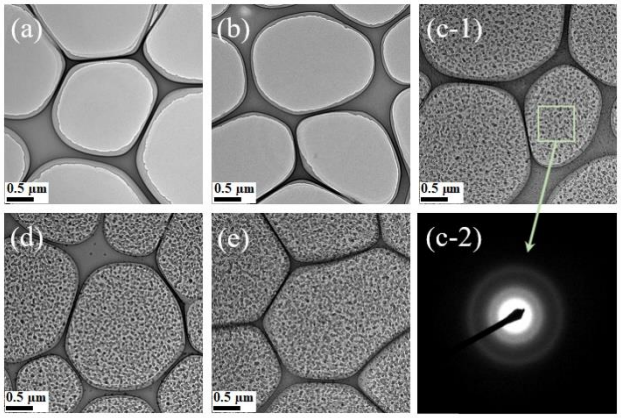

Fig. 2. TEM images of CNPs as a parameter of Ar/CH_4 gas ratio (a) 1:1, (b) 3:1, (c-1) 6:1, (c-2) diffraction pattern of 6:1 (d) 7:1, (e) 9:1.

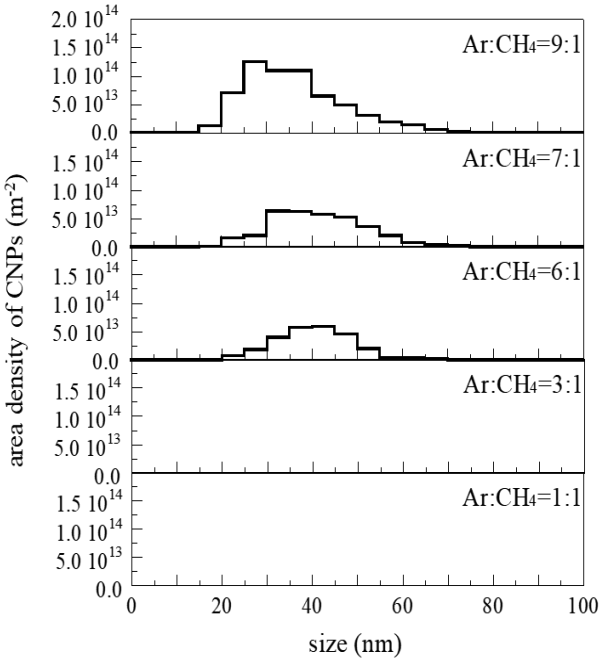

Fig. 3. Area density of CNPs deposited on TEM grids.

size of nanoparticles that exist in the area of 1 μm × 1 μm was measured. The size distribution of CNPs ranges from 5 to 80 nm. With increasing the CH_4 partial pressure, the size of nanoparticles increases, whereas their density decreases. The trend of their density suggests that a possible reason for no nanoparticles for 1:1 and 3:1 is lower nucleation rate for the higher CH_4 partial pressure.

(2) Structure analysis using Raman spectroscopy

Figure 4 shows Raman spectra of the deposited CNPs. The Raman spectra for Ar:CH_4 = 6:1, 7:1, and 9:1 contain two clear peaks, D peak at 1340 cm^{-1} and G peak at 1600 cm^{-1}; while the spectra for Ar:CH_4 = 3:1 and 1:1 have no peak, because no CNPs are deposited on Si substrates, being consistent with the TEM observation in Fig. 3. These peaks signify that the generated nanoparticle has a polymer-like structure that contains sp2 (graphite-like) to sp3 (diamond-like) bonds [9-11]. Moreover, no significant change of the spectra means that the structures of synthesized nanoparticles are nearly identical.

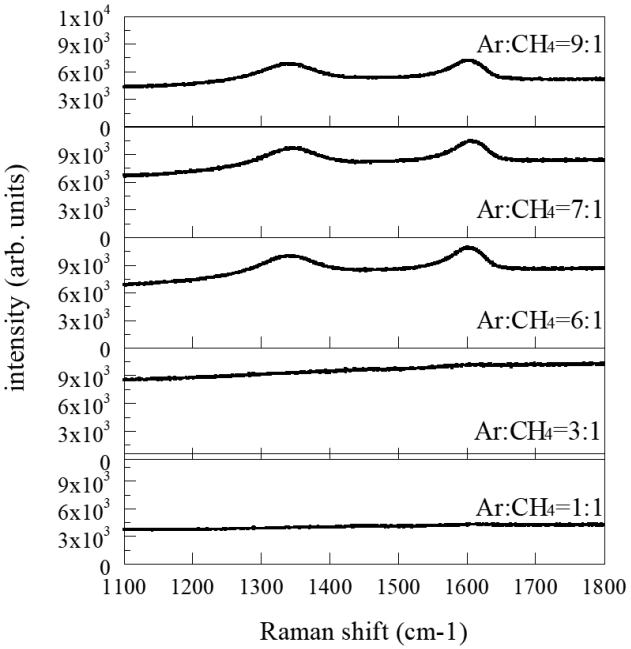

Fig. 4. Raman spectra of CNPs.

4. Conclusions

We have succeeded in continuous synthesis of carbon nanoparticles (CNPs) using a multi-hollow discharge plasma chemical vapour deposition (CVD) reactor with Ar and CH_4 gas mixtures. We examined effects of gas mixture ratio of Ar and CH_4 on the CNPs synthesis. From TEM images, nanoparticles were observed for Ar:$CH_4 \geq$ 6:1. The size distribution of CNPs ranges from 5 to 80 nm. The formed nanoparticles have polymer-like structures that involve sp2 and sp3 bonds. Future study will be carried out to interpret the kinetic relationship between the plasma conditions and the synthesis of nanoparticles.

5. Acknowledgement

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6. References

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