Formation of carbon nanoparticle using Ar+CH₄ high pressure nanosecond discharges

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Abstract. We have studied formation of carbon nanoparticles using Ar+CH₄ high pressure nanosecond discharge non-thermal plasmas. Transition pressure from uniform glow discharges to filamentary ones was clarified to obtain conditions under which uniform glow discharges are sustained. We have produced nanoparticles using the glow discharges, and then we have collected nanoparticles on the grounded electrode by the filtered vacuum collection method. Size distribution analysis reveals that the CH₄ concentration is an important parameter in controlling nanoparticle growth. We have also studied film deposition on the powered electrode and the grounded electrode. The deposition rate on the powered electrode is 7 times higher than that on the grounded electrode. Optical emission observations suggest that radical generation rate near the powered electrode is twice higher than that near the grounded electrode, leading to high deposition rate on the powered electrode.

1. Introduction
Nanoparticles attract a great deal of attention because of their size-dependent properties that differ significantly from properties of bulk materials. Their applications expand into a large number of fields such as environmental, chemical and biomedical engineering [1-4]. So far various kinds of the nanoparticle synthesis methods have been developed [5]. Solution process is one of the succeeded methods but nanoparticles are easily agglomerated in solution without using dispersants, resulting in difficulties of their size control. Moreover, unwanted surface modification such as oxidation occurs with ease in solution. Plasma is a practical method to overcome these problems. Because nanoparticles are charged negatively in plasmas, they tend to grow without their agglomeration. In addition, surface modification of nanoparticles can be controlled by using plasmas. For instance, surface modification of Si nanoparticles has been realized using twin plasmas [6]. Formation kinetics of nanoparticles in low pressure non-thermal plasmas and in high pressure thermal plasmas and their applications have been extensively studied [7-26], while nanoparticle synthesis using high pressure non-thermal plasmas has been attracted relatively little attention. For the high pressure thermal plasmas such as arc plasmas, a large amount of radicals are produced by high density plasmas at high gas pressure and hence productivity of nanoparticles is high. Such high pressure discharges lead to high gas temperature which is one of the major drawbacks for applications to direct nanoparticle deposition to substrates of low melting materials such as organic ones [27]. Although the low pressure non-thermal plasmas are sustained at low gas temperature, they offer rather low productivity of nanoparticles. To overcome difficulties for the low pressure plasma and high pressure thermal plasmas, high pressure non-thermal
plasmas are promising because they can generate high density radicals at high pressure and low gas temperature [28, 29].

In this study, we have studied nanoparticle formation and film deposition using Ar+CH4 high pressure nanosecond discharges to develop a large area process for a high yield nanoparticle synthesis, because nanosecond discharges can generate high pressure non-thermal plasmas.

2. Experimental

Experiments were performed using a nanosecond discharge reactor made of stainless steel. The inner diameter and length of the reactor were 58 mm and 77 mm, respectively. Two pieces of stainless steel electrode of 15 mm in diameter were placed at the center of the reactor as shown in figure 1 [30, 31]. The gap between the powered electrode and the grounded electrode was 0.2 or 0.5 mm. Ar diluted CH4 was employed as ingredient gas, because nanoparticle growth in low pressure CH4 plasmas is quite slow due low gas phase reaction rates of radicals in the plasmas [32] and hence explosive nanoparticle formation in high pressure non-thermal plasmas is expected to be suppressed by the combination of CH4 and nanosecond discharges. Ar gas dilution allows to generate discharges at higher pressure compared to pure CH4. The CH4 concentration was 0.5-100 %. The total gas flow rate was 100 sccm. The total gas pressure was set at 6300 Pa for nanoparticle synthesis. Short voltage pulses were generated using a dc power source equipped with a high speed switch (Behlke HTS-81) and supplied to the upper electrode to generate discharges. Figure 2 shows the typical waveform of discharge voltage and discharge current. The maximum peak discharge voltage was -670 V and the maximum discharge current was -8.8 A. The discharge duration was 280 ns. The repetition frequency was 5 kHz. Although the electrodes were covered by carbon films during CH4 containing discharges, the films had little influence on the shape and peak value of the waveform of discharge voltage and current. We employed nanosecond discharges, because longer duration discharges such as µs discharges tend to be filamentary discharges due to increase of conductivity, and current through the discharge and therefore eventual filamentation.

Nanoparticles deposited on the electrodes were collected by the filtered vacuum collection method, which has been widely employed for dust particle collection in nuclear fusion reactors [33-36]. For the
method, a polycarbonate membrane filter (ADVANTEC K010A) with many holes of 100 nm in diameter was put into a filter holder. The filter holder was set at 0.5 mm above the grounded electrode, then particles on the electrode were sucked for 10 minutes with a rotary pump. The size and shape of the nanoparticles collected on the membrane filter were obtained with a scanning electron microscope (Carl Zeiss Leo 1530). The lower detection limit of size for the SEM measurements was 40 nm.

3. Results and discussion

Our nanosecond discharges are classified into two kinds: uniform glow discharges as shown in figure 3(a), and filamentary discharges as shown in figure 3(b). Uniform glow discharges are generated at lower pressure, whereas filamentary discharges are generated at higher pressure. This is because the larger expansion of the plasma channels and their overlapping tend to take place at the higher pressure. The filamentary discharges are streamers [37]. Glow discharges should be sustained for nanoparticle synthesis to realize production of size controlled nanoparticles in large area. We have studied pressure of transition from glow discharges to filamentary ones to obtain conditions under which the glow discharges are continuously generated. For the measurements, we employed two kinds of electrode surface: metal surface and carbon film surface. Figure 4 shows CH\textsubscript{4} concentration dependence of the transition pressure at which the discharges change from glow discharges to filamentary ones. For carbon film surface electrodes, uniform glow nanosecond discharges are sustained below 1800 Pa in pure CH\textsubscript{4} and below 10000 Pa in pure Ar. Uniform glow discharges tend to be sustained at the lower pressure. They change into filamentary discharges above a transition pressure. The transition pressure increases with decreasing the CH\textsubscript{4} concentration. The transition pressure for the metal surface is higher than that for the carbon film surface. The secondary electron emission coefficient of carbon films deposited on the stainless steel electrodes is 40 % of that of stainless steel [38] and this difference is not important for the discharge mode change. Non-uniformity of electron emission from electrode surface may bring about non-uniformity of current density, namely, filamentary discharges. Carbon films deposited on the electrode surface have low thermal conductivity, low electrical conductivity, and rough microstructure of the surface compared to the bare metal electrode surface. Low thermal

![Figure 3](image-url) **Figure 3.** Photo images of (a) glow discharge and (b) filamentary discharge. Conditions: electrode gap 0.5 mm, CH\textsubscript{4} concentration 5 %, shutter speed 1/100 s.

![Figure 4](image-url) **Figure 4.** CH\textsubscript{4} concentration dependence of pressure of transition from glow discharges to filamentary discharges. Solid circles and triangles indicate the transition pressure below which glow discharges are sustained for carbon film surface electrodes and metal surface ones, respectively. Electrode gap is 0.2 mm.
conductivity tends to enhance localized thermionic emission, low conductivity tends to lead to localized accumulation of charge on the surface, and rough microstructure tends to enhance localized field electron emission. Due to these tendencies, the transition pressure for the metal surface is higher than that for the carbon film surface.

Based on the results mentioned above, we generated uniform glow discharges under the CH$_4$ concentration of 1% and the total pressure of 6300 Pa. Carbon films deposited on the powered electrode are much thicker than that on the grounded electrode. The deposition rate on the powered electrode and the grounded electrode are 0.751 nm/s and 0.107 nm/s, respectively. Since the repetition frequency of the discharges is 5 kHz, the deposition rate per each discharge on the powered electrode and the grounded electrode are 1.50×10$^{-4}$ nm/shot and 2.15×10$^{-5}$ nm/shot, respectively. As shown in figure 3(a), the optical emission intensity near the powered electrode is about twice of that near the grounded electrode, indicating higher generation rate of radicals near the powered electrode, leading to the higher deposition rate on the powered electrode. Based on the assumptions that (1) deposited films are hydrogenated amorphous carbon whose mass density is 1.4 g/cm$^3$ [39] and (2) all carbon containing radicals in gas phase deposit either on the powered electrode or on the grounded electrode, we deduce the lower limit density of carbon containing radicals in gas phase from the deposition rate. The lower limit density is 6.0×10$^{13}$ cm$^{-3}$, corresponding to 0.40% of the initial CH$_4$ concentration. Gas residence time between two electrodes is 1.9×10$^{-2}$ s, whereas the characteristic time of diffusion toward the electrodes is 2.1×10$^{-5}$ s. Therefore, the diffusion is the dominant transport process of carbon containing radicals for the film deposition.

We collected nanoparticles accumulated on the grounded electrode by the filtered vacuum collection method. The nanoparticles collected on the membrane filter were observed with SEM as

![Figure 5. SEM images of (a) membrane filter and (b) nanoparticles collected on the filter. Scale bar indicates 1 µm. Conditions: CH$_4$ concentration 5%, total flow rate 100 sccm, total pressure 6300 Pa, frequency 5 kHz, and discharge time 30 minutes.](image)

![Figure 6. Size distribution of collected nanoparticles as a parameter of CH$_4$ concentration R.](image)
shown in figure 5(b). Collected nanoparticles are classified into three kinds: spherical nanoparticles, agglomerated nanoparticles and flakes. The areal density ratio for these three types is 175:3:4, respectively. Flakes are generated by peeling off deposited films due to internal stress of the films. Although the detail formation kinetics of spherical nanoparticles and agglomerated ones is unclear at present, they are probably generated and grow due to gas phase reactions. Figure 6 shows size distribution of collected nanoparticles as a parameter of CH$_4$ concentration $R$. For $R=2$ %, most nanoparticles are below 150 nm in size. The area density of nanoparticles and their size dispersion tend to be higher and larger for the higher CH$_4$ concentration. These results indicate that CH$_4$ concentration is one of the key parameters in controlling nanoparticle growth.

4. Conclusions
We studied formation of carbon nanoparticles by Ar+CH$_4$ high pressure nanosecond discharge non-thermal plasmas. Following conclusions are obtained in this study.

(1) For carbon film surface electrodes, uniform glow nanosecond discharges are sustained below 1800 Pa in pure CH$_4$ and below 10000 Pa in pure Ar. They change into filamentary discharges above a transition pressure. The transition pressure increases with decreasing the CH$_4$ concentration.

(2) The deposition rates on the powered electrode and the ground electrode center are 0.751 nm/s (1.50×10$^{-4}$ nm/shot) and 0.107 nm/s (2.15×10$^{-5}$ nm/shot), respectively for the CH$_4$ concentration of 1% and the pressure of 6300 Pa. The spatial profile of optical emission intensity suggests that radical generation rate near the powered electrode is much higher than that near the grounded electrode, leading to the unbalance of deposition rate on these two electrodes.

(3) Nanoparticles are produced by the nanosecond discharges. For the CH$_4$ concentration of 2%, most nanoparticles are below 150 nm in size. The area density of nanoparticles and their size dispersion tend to be higher and larger for the higher CH$_4$ concentration. These results indicate that CH$_4$ concentration is one of the key parameters in controlling nanoparticle growth.

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