Production and transport of carbon nanoparticles in high-pressure magnetron sputtering plasmas employing a graphite target

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Abstract ? The formation of carbon nanoparticles was observed in the gas phase of a magnetron sputtering plasma employing a graphite target, argon gas, and a dc power supply, when the plasma source was operated at a pressure higher than 200 mTorr. Nanoparticles were accumulated in the region just outside of the bright plasma. A part of nanoparticles leaked out from the accumulated region, and was transported toward the downstream side. When the electric potential of the substrate, which was placed in the downstream region, was floating, nanoparticles were trapped by the sheath electron field and were not transported to the substrate. When the substrate was biased at +15 V with respect to the ground potential, nanoparticles were transported efficiently to the substrate

INTRODUCTION

Magnetron sputtering discharges are usually operated at low gas pressures such as 3 mTorr when they are used for depositing thin films of target materials. In this work, we used a conventional magnetron sputtering plasma source for synthesizing nanoparticles of the target material by increasing the discharge pressure above 100 mTorr. According to gasphase diagnostics of a magnetron sputtering plasma by laser-induced fluorescence [1-3], the density distribution of atoms ejected from the target is localized near the target surface in a high-pressure discharge. Since the collision between ejected atoms are enhanced by the localized density distribution, the growth of nanoparticles in the gas phase is possible in a high-pressure discharge. In this work, we employed a graphite plate as the target material for synthesizing carbon nanoparticles. The characteristics of the synthesis and transport of carbon nanoparticles were investigated in various plasma conditions.

EXPERIMENT

The experimental apparatus is schematically shown in Fig. 1. A vacuum chamber with four large observation ports had a diameter of 16 cm and a length of 18 cm. A conventional magnetron sputtering source with a pair of cylindrical permanent magnets on an indirect water-cooling system was inserted from the top of the vacuum chamber. A graphite target with a diameter of 50 mm was installed on the cathode.

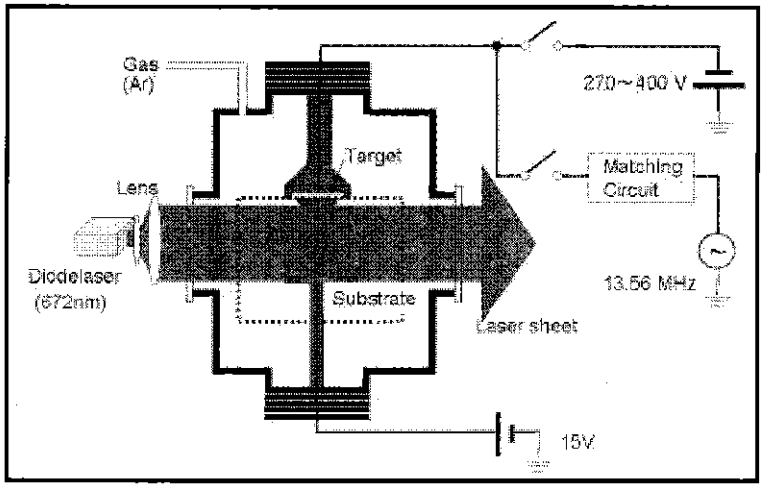

Figure 1: Experimental apparatus.

The cathode was surrounded by a ring grounded electrode which was used as the anode of the discharge. The cathode was connected to a dc power supply. We also used an rf power supply at 13.56 MHz for the sake of comparison. The discharge power was 4-60 W in the case of the dc discharge and was 10 W in the case of the rf discharge. The discharge gas was pure Ar, and the gas pressure was measured using a capacitance manometer. A stainless steel substrate was placed at a distance of 6.5 cm from the target. The substrate was connected to a dc power supply.

To monitor the generation and the transport of nanoparticles, the discharge space was illuminated by a planar cw laser beam yielded from a diode laser at 672 nm. The two-dimensional image of the laser light scattered by nanoparticles was captured using a CCD camera with an image intensifier. We examined the size and the surface density of nanoparticles on the substrate using a scanning electron microscope (SEM).

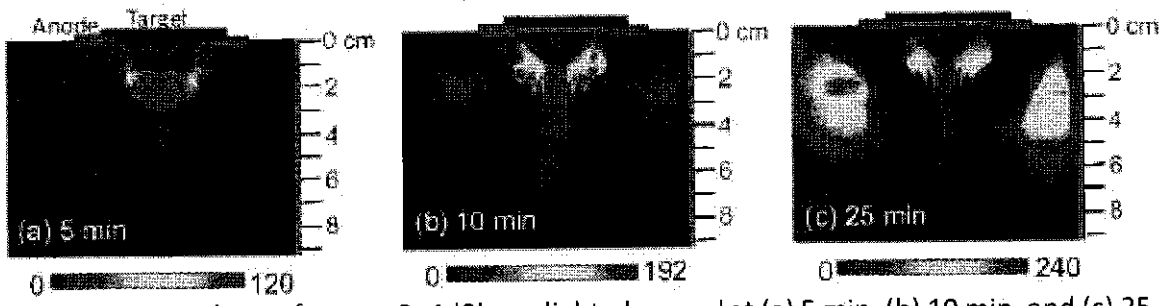

Figure 2: Snap shots of scatter2e4d0laser light observed at (a) 5 min, (b) 10 min, and (c) 25 min afterthe initiation of a discharge at an rf power of 9.3 W and a pressure of 500 mTorr.

SYNTHESIS CHARACTERISTICS OF CARBON NANOPARTICLESIN THE GAS PHASE

3.1 Temporal evolution

We observed slow evolution of carbon nanoparticles after the initiation of the discharge. Figure 2 shows pictures of the scattered laser light at various delay times after the initiation of a discharge at an rf power of 9.3Wand a pressure of 500 mTorr. The locations of the target (the cathode) and the ring anode is illustrated in the figure. At the beginning of the discharge, we observed no scattered laser light from the discharge region. Figure 2(a) shows the distribution of the scattered laser light observed at 5 min after the initiation of the discharge. It is noted that this experiment used a conventional magnetron sputtering source, in which a bright plasma driven by the $E \times B$ drift of electrons is localized in the vicinity of the target surface. Figure 2(a) indicates that the growth of nanoparticles occurred in the region outside of the bright plasma.

At 10 min after the initiation of the discharge, as shown in Fig. 2(b), the scattered laser light from the region below the bright plasma became stronger (it is noted that the maximum intensity of the scattered laser light is deferent in Figs.2(a)-2(c) as shown by the scales below the pictures). In addition, it was observed that a part of nanoparticles leaked out from the accumulated region toward the downstream side as shown in Fig. 2(b). The flow velocity of nanoparticles evaluated from a movie of the scattered laser light was approximately 1.4 cm/s. At 25 min afterthe initiation of the discharge, as shown in Fig. 2(c), the accumulation of nanoparticles was also observed in the peripheral region of the vacuum chamber. The leak and the transport of nanoparticles toward the downstream side was also observed at 25 min afterthe initiation of the discharge. It should be emphasized again that we observed no scattered laser light from the bright plasma region even at long delay times.

3.2 Dependence on discharge conditions

The synthesis efficiency of carbon nanoparticles was significantly dependent on the discharge pressure, and we detected scattered laser light only when the discharge pressure

was higher than 200 mTorr. In addition, it was found that the synthesis efficiency and the spatial distribution of carbon nanoparticles were dependent on the discharge power. Figure 3 shows distributions of the scattered laser light observed at a pressure of 400 mTorr. At a low discharge power of 8.1 W, as shown in Fig. 3(a), nanoparticles were accumulated in the region just outside of the bright plasma, and a part of nanoparticles leaked out from the accumulated region toward the downstream side. On the other hand, at a high discharge power of 60 W, nanoparticles are mainly located in the periphery region of the vacuum chamber, and the transport of nanoparticles toward the downstream region was not observed as shown in Fig. 3(b). Therefore, it can be said that a low-power discharge is suitable for depositing nanoparticles on a substrate placed in the downstream region.

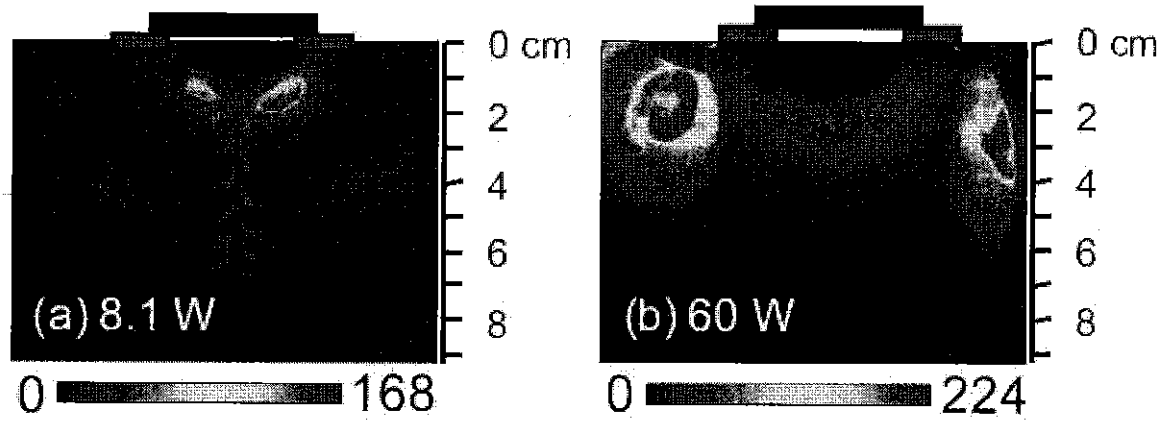

Figure 3: Distributions of scattered laser light observed at discharge powers of (a) 8.1 and (b) 60 W. The pressure was 400 mTorr.

TRANSPORT OF NANOPARTICLES TOWARD A SUBSTRATE

Figure 4 shows pictures of scattered laser light when a stainless-steel substrate is placed at a distance of 65 mm from the target. The discharge power and the gas pressure were 4 W and 400 mTorr, respectively. It is noted that the emission from the plasma is not subtracted in these pictures (the picture shows the superposition of the plasma emission and the scattered laser light).

Figure 4(a) was obtained when the electric potential of the substrate was floating. We detected no scattered laser light in the vicinity of the substrate surface. It was observed that nanoparticles leaked out from the production region were not transported to the substrate. This is because nanoparticles in plasmas have negative charges. In the case ofthe floating substrate, the transport of negatively charged nanoparticles toward the substrate, which has negative potential with respect to the plasma potential, is impossible. The position where nanoparticles are trapped is determined by the balance between the electrostati c force and the gravity.

Figure 4(b) was obtained when the substrate was biased at +15 V with respect to the ground potential. In this case, we observed the transport of nanoparticles toward the substrate surface, since the potential of the substrate was positive with respect to the plasma potential. Such a control of the transport of nanoparticles is possible since the plasma potential is well defined by the potential of the grounded anode in the dc discharge, and the plasma potential is not affected by the bias voltage applied to the substrate.

For the sake of comparison, we carried out the same experiment by replacing the dc power supply with an rf power supply. It was observed that the production efficiency of nanoparticles in the rf discharge was higher than that in the dc discharge. However, the transport of nanoparticles toward the substrate was difficult in the case of the rf discharge even when a positive bias voltage was applied to the substrate. It was observed that nanoparticles were trapped in the sheath electric field, indicating that the plasma potential is affected by the voltage applied to the substrate. Although the rf discharge has potential for rapid deposition of nanoparticles because of the efficient production in the gas phase, we have to develop a method, by which the plasma potential is not affected by the bias voltage to the substrate.

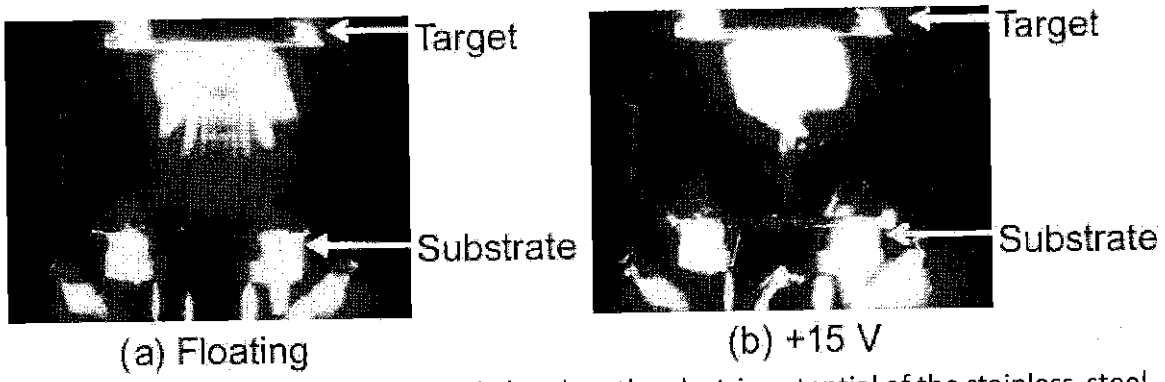

Figure 4: Pictures of scattered laser light when the electric potential of the stainless-steel substrate was (a) floating and (b) +15 V with respect to the ground potential.

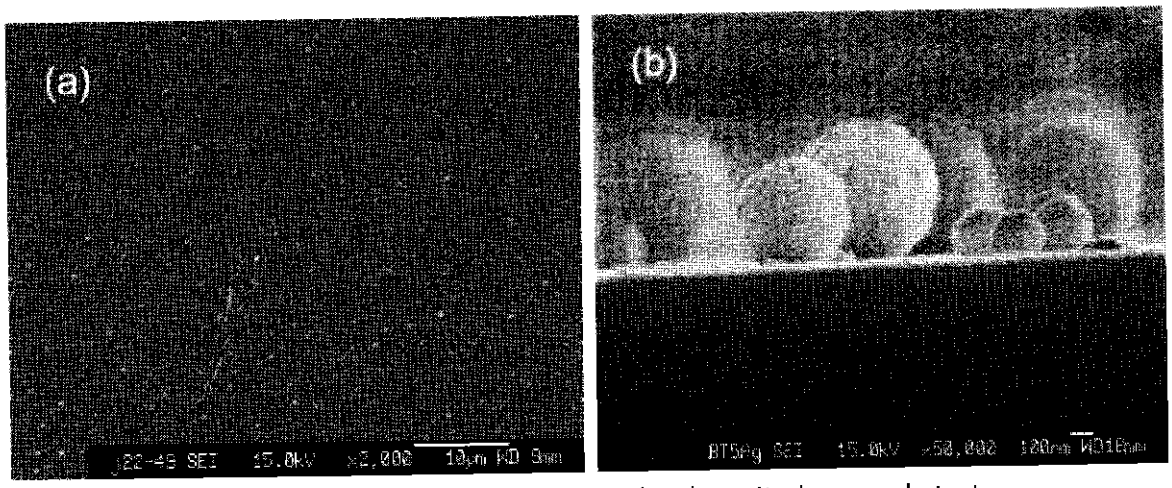

Figure 5: SEM pictures of nanoparticles deposited on a substrate.

NANOPARTICLES ON THE SUBSTRATE

We succeeded in depositing nanoparticles on the substrate by applying the positive bias voltage. Figure 5 shows SEM pictures of nanoparticles deposited on the substrate. The sizes of nanoparticles were roughly from 200 to 800 nm. The surface morphology of nanoparticles suggests that nanoparticles observed by SEM are formed by the condensation of smaller nanoparticles and clusters in the gas phase. The density of nanoparticles on the substrate surface is sufficient for applying them to a nanocomposite film.

CONCLUSIONS

We have shown that a magnetron sputtering plasma source is applicable for synthesizing carbon nanoparticles by operating it at a pressure higher than 200 mTorr. Nanoparticles produced in the gas phase of the magnetron sputtering discharge can be transported toward the substrate by adjusting the discharge power and by applying a positive bias voltage to the substrate. We will apply nanoparticles thus synthesized to a nanocomposite thin film.

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