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Carbon Nanotube Synthesis using Magnetic Null Discharge Plasma Production Technology

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Abstract – Carbon nanotube (CNT) properties, produced using a magnetic null discharge (MND) plasma production technology, were investigated. We firstly deposited the Fe layer 200 nm in thickness on Si substrate by the magnetic null discharge sputter method at the substrate temperature of 300oC, and then prepared CNTs on the catalyst layer by using the magnetic null discharge (MND) based CVD method. CNTs were deposited in a gas mixture of CH4 and N2 at a total pressure of 1 Torr by the MND-CVD method. The substrate temperature and the RF power were 650oC and 600 W, respectively. The characterization data indicated that the proposed source could synthesize CNTs even under relatively severe conditions for the magnetic null discharge formation.

Keywords : Carbon nanotubes, Magnetic null discharge plasma, Plasma enhanced chemical vapor deposition, Single-line plasma process, Sputtering

1. Introduction

Reports of the synthesis and identification of carbon nanotubes (CNTs), both single-walled [1] and multi-walled [2], have excited great interest in the field of carbon and related materials studies. Extraordinary properties, such as electronic [3] and mechanical [4] properties, have been performed both theoretically and experimentally. It has also been an important issue to search for new processing techniques, especially in the low temperature regime, which can produce high-quality CNTs in large quantities, while allowing control of the fabrication process with ease and precision. A number of techniques have been used to synthesize CNTs including arc discharge method [1-4], chemical vapor deposition (CVD) [5], laser ablation [6], etc. However, it has been shown that plasma enhanced chemical vapor deposition (PECVD) [7] is one of the most promising techniques for low temperature deposition, high deposition rate, cleanliness and low particulate levels. For low temperature deposition the operating gases need to be activated using a microwave, laser, radio frequency (RF) or DC plasma to achieve respectable growth rates. Without this enhanced precursor activation, extreme substrate temperatures are required, and this severely limits the number of potential applications. With these considerations in mind, a magnetic null discharge (MND) plasma enhanced chemical vapor deposition (MND-CVD) apparatus has been set up in an effort to seek new processing routes for high-quality and high-efficiency CNT production. This new system incorporates aspects of physical and chemical vapor deposition using capacitively coupled RF plasma production technology and magnetic confinement coils. The capacitive coupled RF plasma source plays the role of sputtering for Fe catalyst layer formation. The confined high-density plasma with magnetic field could affect the properties of CNTs in the CVD process. Magnetic null discharge (MND) plasma has been proposed as a new plasma source which satisfies the above requirement [8-11]. The key to the MND plasma production is the formation of magnetic null (MN) region, which can easily be controlled by varying currents in magnetic coils. Electrons around the MN region move in a nonlinear manner with effective electron heating whereby high-density plasma can be obtained. In the field of etching applications, good results have already been reported [11, 12]. Incidentally, carbon nanotube (CNT) growth is commonly carried out using plasma enhanced chemical vapor deposition (PECVD), and the process can easily be applied to industrial production lines. Additionally, the catalyst deposition is an auxiliary step in PECVD for the CNT growth, and is commonly performed in a separate chamber. In this work, a single-chamber plasma process technology based on the MND concept was proposed for the application of CNT growth. Namely, this article focused on whether the proposed system based on the MND concept was useful to synthesize CNTs.

2. System Geometry and description

As shown in Fig. 1, the MND-CVD incorporates aspects of physical and chemical vapor depositions for the single line process where a capacitive coupled MND sputter system [13] and an antenna-type MND system are combined.

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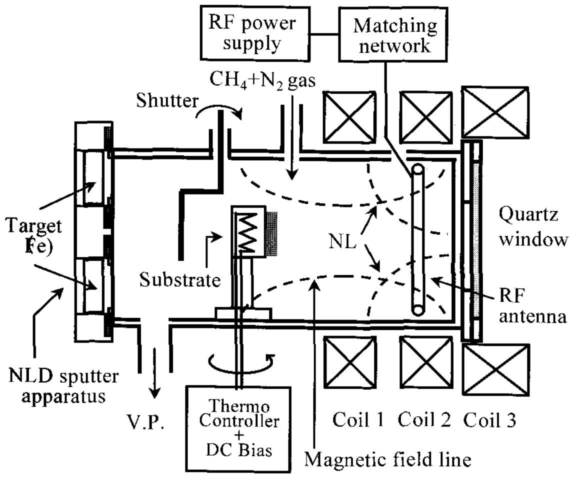
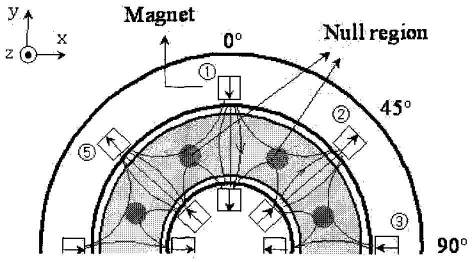


Fig. 1. Experimental setup of the combined sputter / PECVD chamber for CNT growth

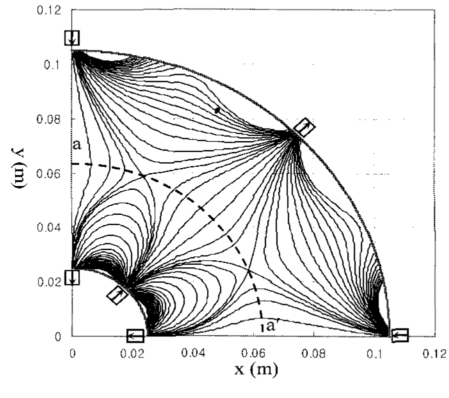
This dual sputter/PECVD process was used for catalyst deposition in situ, followed by CNT growth. The chamber was made of stainless steel with an internal diameter of 308 mm. An MND sputter source, specially designed for catalysts formation, has been described in detail in our previous reports [13, 14], and can be briefly summarized as follows. The system consisted of 8 pairs of permanent magnets arranged circularly. The array of magnets formed eight null regions perpendicular to the Fe target surface. The Fe target was in doughnut shape 70 mm in width. The distance between the Fe target and a substrate was 200 mm. Cooling water was circulated through the target to prevent overheating. The ring-typed outer magnetic holder could be rotated at intervals of 5° during deposition for controlling the magnetic null field dynamically. By the rotation of the magnetic field, the enhancement of target erosion and film uniformity were possible. Thus, in the application of MND plasma, controlling of the position and the diameter of the magnetic null region can easily be achieved, which realizes the uniform processing as well as the successful reduction of plasma localization from the wall effect.

Fig. 2 shows the arrangement of the permanent magnets and the calculated magnetic field on the target surface in a sector of 90 (from 0 to 90). Four adjacent magnet groups with the same magnetic field strength formed the MN regions at the center of the plane containing the magnets. MN regions, as seen in Fig. 2(b), are formed at (64.3 mm, 22.5°) and (64.3 mm, 67.5°) from the target surface in the z direction, and the B=0 line can be seen formed. In an antenna-type MND source whose structure and concept were also detailed in previous reports [15, 16],

A p-type Si (100) wafer 50 mm in diameter was used as a substrate, which was arranged on a substrate holder. The substrate holder was designed to allow the rotation and then both sputtering and CVD could be performed in single line process. The formation of iron oxygen compounds on the Fe catalyst layer deposited by MND sputter method were evaluated by ex situ XPS in advance. From the result of XPS spectral profiles of O (1s) detected on the catalyst (pre/post surface treatments), FeO peak always appeared after air exposure and could be erased by in situ plasma surface treatment. This suggests that the Fe catalyst layer is easily exposed to air prior to CNT deposition because catalyst growth and CNT growth are commonly done in separate chamber. The oxygen contamination affects the CNT growth and properties, even if a pre-treatment of the ex situ deposited catalyst layer is done. Thus, our used substrates were in situ prepared by MND sputter method followed by MND-CVD.



(a) Arrangement of permanent magnets



(b) Magnetic field in a sector of 90°

Fig. 2. Magnetic field distribution on the target

3. Experimental Procedures

High quality single and multi-walled CNTs can be obtained on adequate catalysts and that their size and distribution determine the characteristics of CNTs. Incidentally, Fe catalysts serve as the nucleation sites for the growth of CNTs due to their active catalytic function. In this work, an Fe catalyst layer 300 nm in thickness was deposited from the Fe target on the p-type Si wafer by MND sputtering. The deposition was carried out in Ar gas at pressure of 5.0×10^{-2} Torr. The substrate temperature, RF power, and deposition time were 300°C, 400 W, and 20 min, respectively. After the Fe deposition, the plasma chamber was purged for a few minutes with flowing nitrogen gas to carry out *in situ* plasma surface treatment on the Fe catalyst layer using the antenna-type MND. The formation of uniformly distributed high-density nano-sized catalysts is very important for high quality CNT growth because each nano-scale Fe particle works as the active catalyst for the nucleation of CNTs. Therefore, the plasma surface treatment was carried out for the purpose of not only erasing the oxygen component on the Fe catalyst layer but also for reforming the nano-scale Fe catalysts. In this case, the RF power was set at 400 W, while maintaining the gas pressure at 5.0×10^{-2} Torr. The substrate temperature and the plasma treatment time were set at 600°C and 20 min, respectively. The magnetic flux density near the substrate surface was about 150 G. By introducing the magnetic field to the substrate, the plasma generated intensively near the MN region spread toward the substrate along the magnetic field line, and thus the Fe layer on the substrate was subjected to a flux of bombarding ions sufficiently to cause changes in the surface structure. Regarding CNT synthesis on Fe catalysts, the fabrication conditions using MND-CVD were summarized as follows. The CNTs were prepared in a gas mixture of 40% CH4 and 60% N2 at a total pressure of 1 Torr with Fe/Si substrate temperature of 600°C and RF power of 600 W. The current of the three coils were set as I_1=48 A, I_2=48 A, and I_3=24 A. Deposition process was performed for 60 min. SEM, TEM, and RS evaluated the properties of the obtained CNTs.

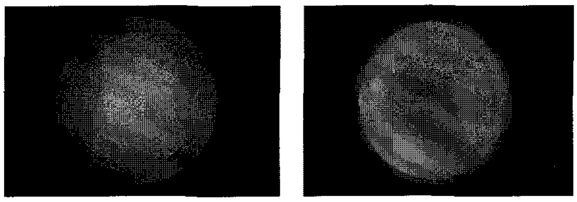
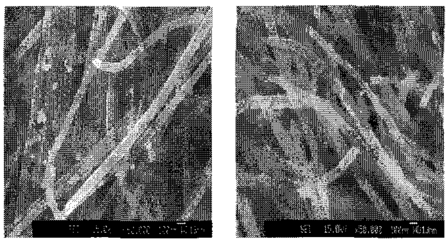

(a) N2–CH4 (20%), P_{RF}=400W (b) N2–CH4 (40%), P_{RF}=600W

Fig. 3. MND plasma images taken for N2–CH4 gas mixtures


(a) N2–CH4 (40%) (b) CH4 (50%)


(c) N2–CH4 (60%)

Fig. 4. SEM images of CNTs synthesized by MND-CVD for various CH4 ratios of (a) N2–CH4 (40%), (b) N2–CH4 (50%) and (c) N2–CH4 (60%)

4. Results and Discussions

Fig. 3(a) and 3(b) show the images of MND plasma taken for CVD conditions as mentioned above. The optical emission spectra in these conditions were also observed by CCD camera. In the spectrum of Fig. 3(b), one can observe the characteristic emission of CH radicals (390 and 430 nm) and C2 components (515 and 560 nm). It can be seen from the spectral measurements that intensities of N2-related optical emission spectral lines are nearly independent of position, while intensities of optical emission spectral lines associated with CH and C2 are significantly higher near the plasma periphery areas. When CH4 ratio exceeds about 40%, the intense orange–yellow emission is observed in the plasma region of high emission. The uniform synthesis with the area of several cm^2 could be obtained. Figures 4(a), 4(b), and 4(c) show the SEM images of CNTs synthesized using MND-CVD for CH4 ratios of 40, 50, and 60%. As shown in Figs. 4(a) and 4(b), comparatively high density CNTs of 10 μm in length grow on the Fe/Si substrate. The synthesis rate of CNTs was 166 nm/min. Incidentally, some carbonaceous particles or clusters are observed in CNTs for the case of CH4 ratio=60%. Such carbonaceous particles and clusters were formed when CH4 ratio was more than 55%, and this is independent on other deposition parameters such as the substrate temperature and RF power.

Fig. 5 presents the TEM image of the CNT sample deposited for CH4 ratio=40. The TEM image shows the hollow core in a repetitive arrowhead shape. For the case of CH4 ratio=40%, the tip of the arrowhead is in the range of 10-20 nm while the wide side of the arrowhead is in the range of 15-30 nm. The CNTs have an outer diameter of about 95 nm, and the wall thickness is in the range of 65-85 nm. The tubule is composed of about 50 graphene shells. For the case of CH4 ratio=60%, the innermost layer is discontinuous and terminated at several positions. This indicates uncompleted CNTs growth of the innermost shell.

Fig. 6 shows the single phonon (first order) Raman spectra, which were obtained using visible photons (e.g. 514.5 nm from the Ar+ ion laser) focused on CNT samples with a beam size of 20 mm using a Raman microscope. The CNT samples were obtained at CH4 ratio=40 and 60%. The most dominant feature of both samples almost agrees. There are two peaks at 1349.8 cm^{-1} (D-band) due to microcrystalline graphite and 1575.3 cm^{-1} (G-band) due to crystalline graphite. The intensity of the D-band peak is lower than that of the G-band. It is known that the peak at 1349.8 cm^{-1} indicates the existence of carbonaceous particles

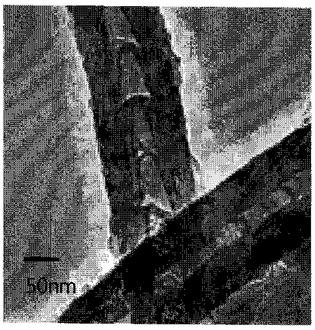


Fig. 5. TEM image of the CNTs deposited for CH4 ratio = 40%

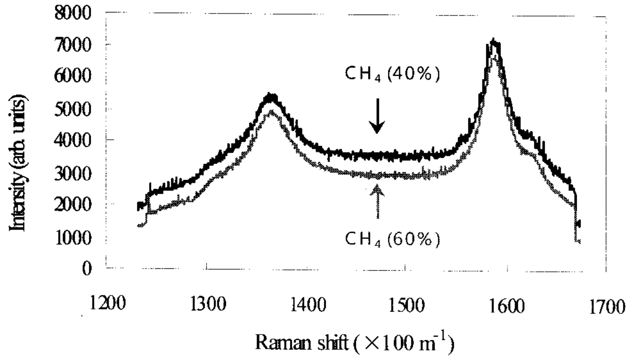


Fig. 6. Raman spectra of CNTs deposited by MND-CVD at CH4 ratio=40 and 60%

defected from the curved graphitic sheet and tube ends [17]. Thus, the results indicated that our proposed PECVD system based on MND concept could synthesize CNTs although their qualities were insufficient. However, this article focused on whether the MND-CVD system was useful to synthesize CNTs. The deposition was performed only under some discharge conditions. The MN radius was fixed at 100 mm. Additionally, there was a distance of 230 mm between the substrate and the MN. To synthesize CNTs efficiently, a large number of radicals are required on the substrate. One of special merits of the MND plasma is to obtain the high-density plasma even at low pressure, which is sustained by nonlinear motions of electrons around the MN. However, the operating pressure in this work was high and therefore effective electron heating was probably insufficient. Consequently, the radical supply from the MN plane 230 mm apart from the substrate was insufficient. In other words, the depositions were performed under relatively severe conditions for the MND formation. A drive system of the substrate in the z direction should be added and thereafter we should perform the deposition at lower pressure.

5. Conclusion

A hybrid PECVD system based on the MND concept was proposed for the single-line process of the CNTs growth. It was confirmed that our proposed system could synthesize CNTs although the depositions were performed under relatively severe conditions for the MND formation. The MND plasma can produce the high density plasma even at low pressure and perform a large surface area processing by controlling the MN. Further improvements of quality and the synthesis rate can be promoted by optimizing the MND formation condition and drive system of the substrate. Studies in these directions are now in progress. Additionally, further CNTs research for semiconductor technology and fuel cell application is ongoing.

Acknowledgements

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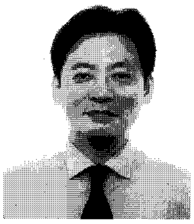

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