Comparison of Plasma Parameters in CCP and ICP Processes Appropriate for Carbon Nanotube Growth

Yohei SAKAMOTO, Shuichi MAENO [1)], Nobuteru TSUBOUCHI [2)]
Toshiro KASUYA and Motoi WADA

Graduate School of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan
[1)] *Novelion Systems, Co. Ltd, Kyotanabe, Kyoto 610-0332, Japan*
[2)] *AIST Kansai, Advanced Industrial Science and Technology, Ikeda, Osaka 563-8577, Japan*

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Vertically aligned carbon nanotubes (CNTs) were grown on Si substrates by radio frequency (RF) plasma enhanced chemical vapor deposition. We investigated plasma conditions suitable for CNT growth by measuring plasma parameters and observing optical emission spectrometry near the substrate. Comparison in plasma parameters was also made between a capacitively coupled plasma (CCP) and an inductively coupled plasma (ICP) excited in an identical plasma reactor. The measured electron temperature of CCP was higher than that of ICP, while the electron density of CCP was smaller than that of ICP. Vertically aligned CNTs were produced with -10 V bias to the substrate for CCP, while they were produced with bias more negative than -200 V for ICP.

Keywords: CNT, plasma enhanced chemical vapor deposition, Langmuir probe, optical emission spectrometry, capacitively coupled plasma, inductively coupled plasma

1. Introduction

Carbon nanotubes (CNTs) discovered in 1991 by Iijima [1] have various potential applications such as field emission displays [2], tips for atomic force microscope [3], and electronic memory devices [4] due to their unique electrical and mechanical properties. There are many methods to grow CNTs, and plasma enhanced chemical vapor deposition (PECVD) is considered as one of the most promising methods for preparing a vertically aligned CNTs on a substrate. This method can produce CNTs at relatively lower temperature, and can control diameter and length of produced CNTs over a large area. Among several types of PECVDs, radio frequency (RF) excited capacitively coupled plasma (CCP), and inductively coupled plasma (ICP) have been used in many industrial applications, because these methods are simple to construct and easy to scale up.

In controlling CNTs growth with PECVDs, plasma parameters, or electron temperature and density, are important. It is possible to change the growth condition for CNTs in a specific system by controlling plasma parameters, and effects upon CNTs growth resulting from change in hydrocarbon radicals and ion concentrations correlated to plasma parameters have already been reported. However, these reports dealt with only one type of RF system, and effects upon CNTs growth condition due to change from CCP to ICP system has not been studied yet. In this paper, we report the difference between CCP and ICP discharges in plasma parameters using a Langmuir probe, and that in concentration of hydrocarbon radicals by optical emission spectrometry (OES). The effects upon CNTs growth are discussed by comparing the results from these measurements.

2. Experimental details

The schematic diagrams of CCP and ICP systems are shown in Fig. 1 and Fig. 2, respectively. A RF power was supplied through a 52 mm diameter stainless steel electrode in CCP configuration. Ring shaped Sm-Co magnets and cylindrical Sm-Co magnets were mounted in the electrode to form a planar magnetron magnetic field geometry for effective production of high density plasma near the electrode. An ICP discharge was established by a 5 turns 2 mm diameter copper coil wound outside of a 90 mm diameter 100 mm long quartz tube.

A movable Langmuir probe was designed to measure spatial distributions of plasma parameters near the CNT deposition substrate. The center conductor of the probe was 0.3 mm diameter tungsten wire exposing 2 mm-long tip to the plasma. This center conductor was insulated by 1 mm outer diameter 0.4 mm inner diameter alumina tube. The probe is inserted into a 1.5 mm outer diameter 1.2 mm inner diameter copper tube connected the ground to realize noise shielding. This copper tube was further shielded with a 3 mm outer diameter 2 mm inner diameter alumina tube to protect the copper tube

Corresponding author; E-mail address: mwada@mail.doshisha.ac.jp

against radiation from plasma. This probe rotated in the chamber to be set at any radial distance from the center, and can measure radial distributions of plasma parameters near the Si substrate to hold grown CNT. Probe voltage was controlled by GPIB controller, and current-voltage characteristics were recorded by digital multi meters coupled to a computer. In our probe measurement, all distributions of plasma parameter were measured for Ar plasmas with the identical discharge condition with H_2 diluted CH_4 plasma, as insulating film was formed on the electrode of the Langmuir probe by continuous operation.

An optical multi-channel analyzer (OMA; Hamamatsu Photonics model PMA-11) measured the optical emission spectrum (OES) of light emitted from a plasma near the Si substrate. The line of sight was set parallel to the Si substrate, and the light was delivered to the OMA through an optical fiber. Signal integration times were adjusted to be the same for both CCP and ICP.

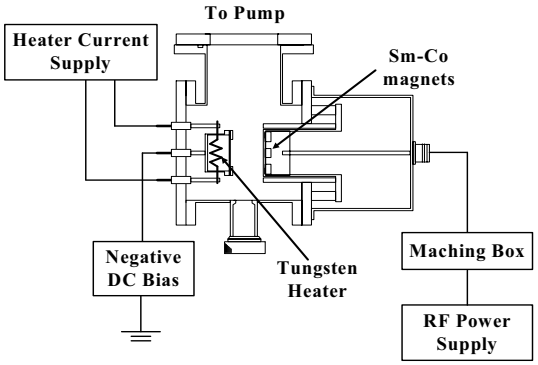

Fig.1. Schematic diagram of experimental apparatus of CCP.

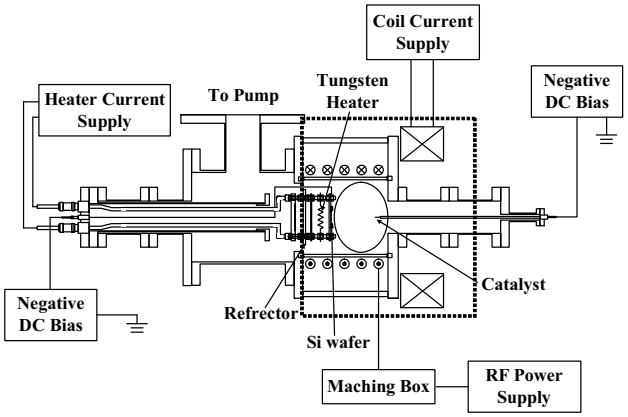

Fig.2. Schematic diagram of experimental apparatus of ICP.

Negative DC voltage against the ground and electrical current for a heater to control the temperature of the Si substrate were supplied to the substrate and a tungsten heater mounted at the backside of the Si substrate, respectively. Electrical connections to the substrate and the heater were made through hermetic electrical current feed-throughs welded on a flange holding the CNT substrate. The substrate heater consisted of a 0.6 mm diameter tungsten wire and heated Si substrate up to 830 K by infrared radiation.

After cutting a P type (1 1 1) single crystal Si wafer into a 16X16 mm^2 square sample, the sample was cleaned with ethanol and put into the Si substrate holder. After evacuating the chamber down to a pressure lower than $1X10^{-3}$ Pa, a 50 mm X 20 mm Ni sheet metal was introduced into the plasma reactor. Applying negative voltage to the sheet metal in a plasma, Ni catalyst was deposited on a Si substrate by sputtering. The sheet metal was removed from the plasma reactor, and the temperature of the Si substrate was maintained for 30 minutes to form Ni nano particles of proper size for CNTs production as a pretreatment [5]. Methane and hydrogen were introduced into the chamber, and their partial pressures were kept constant by regulating gas flow rates with needle valves. A RF power generated a plasma for CNTs growth for fixed duration. The sample was taken out of the substrate holder after cooling. The produced samples were observed by a field emission scanning electron microscope (JEOL, JSM7000FD).

3. Experimental results

3.1 Spatial distribution of plasma parameters

After introducing 5 Pa Ar gas to the system, the plasma was generated by a RF power. The Langmuir probe was moved from the center of the Si substrate to the chamber edge. The distance from the center to the edge was 60 mm for CCP, and 45 mm for ICP apparatuses, respectively. Probe voltage was changed from -10 V to +15 V with respect to the chamber wall at an interval of 0.1 V, and probe current was recorded by measuring the voltage across a 1 kΩ resistor to determine electron temperature and density.

The measured distribution of electron temperature and that of electron density for CCP operation are shown in Fig. 3(a) and Fig. 3(b), respectively. Those for ICP are shown in Fig. 4(a) and Fig. 4(b), respectively. Comparing the plasma parameters for both discharges, electron temperature of CCP was higher than that of ICP. As the probe tip position came closer to the edge, electron temperature of ICP increased, while that of CCP decreased. High energy electrons were expected localized near the edge of ICP, as the RF power was supplied from inductive coils outside of the glass vessel. At the edge of CCP apparatus, magnetron magnetic field was weak and high energy electrons were not confined there. Meanwhile, electron density of ICP appears to be about 10 times as large as that of CCP. Electron density profile of ICP is flat while that of CCP decreased rapidly, as the probe moved toward the edge.

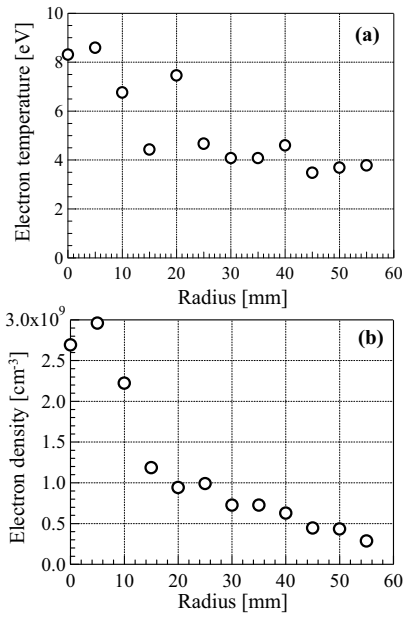

Fig.3. Radial distributions of plasma parameters of CCP. (a) electron temperature, (b) electron density.

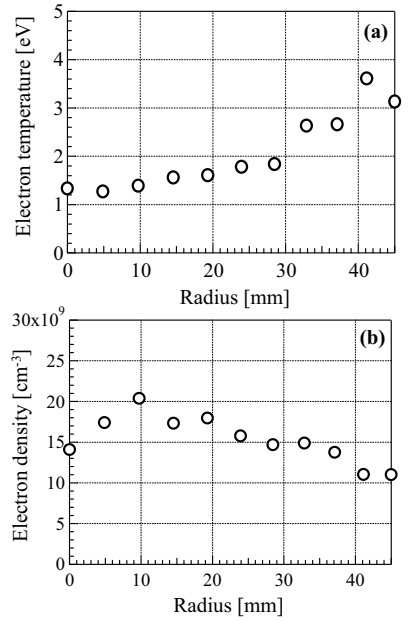

Fig.4. Radial distributions of plasma parameters of ICP. (a) electron temperature, (b) electron density.

3.2 OES of radicals and ions

To measure hydrocarbon radicals and ions present in a plasma, an optical fiber connected to the OMA was mounted for OES measurement. After 4 Pa methane and 1 Pa hydrogen were introduced into the chamber, a plasma was generated with each type of discharge. Results for both discharges are shown Fig. 5. The upper spectrum was obtained with ICP discharge, while the lower spectrum was taken with CCP. The emission intensity of ICP was about 15 times as high as that of CCP. When an intensity ratio of each spectrum is normalized to H_α (656 nm), which shows the highest intensity, line spectrum of 516 nm in the C_2 swan band [6,7] is the only line exhibited a characteristic difference beween ICP and CCP. In other spectral range of C_2 band and CH band, no appreciable difference was observed for the plasma conditions appropriate for CNTs growth.

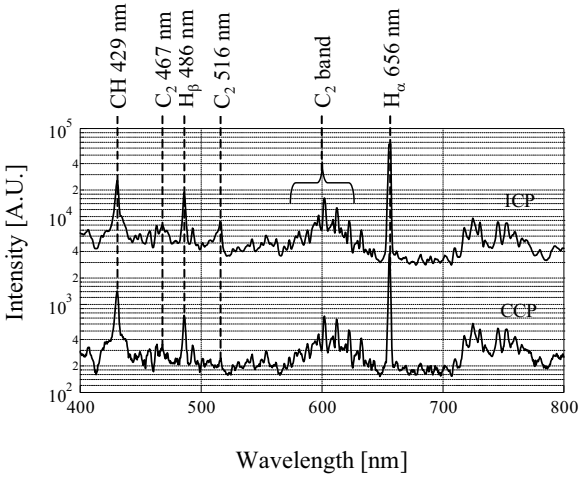

Fig.5. Optical emission spectra of methane and hydrogen plasma by CCP and ICP discharge.

Change in OES intensity ratios of CH at 390 nm, CH at 429 nm, C_2 at 467 nm, H_β at 486 nm and C_2 at 516 nm normalized to H_α were investigated by varying the RF power. Ikuno *et al.* [8] reported that CH and H_β intensity ratios normalized to H_α depended on RF power applied to their CCP discharge. We measured the power dependence of OES by using our ICP discharge. Intensity ratios of hydrocarbon radicals and ions normalized to H_α are shown Fig. 6. Our results are similar to those by Ikuno *et al*., and show maximum intensities at RF power of 100 W. All intensity ratios gradually decreased, as the RF power was further increased from 100 W.

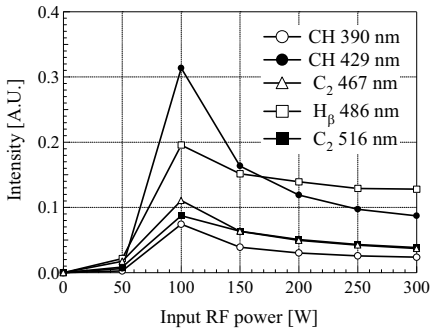

Fig.6. Intensity ratio of each line spectrum normalied to H_α as a function of input RF power.

3.3 Grown carbon nanostructures

The condition for CNTs growth was observed for both RF discharges by varying negative DC bias applied to the Si substrate. Structures of carbon films prepared

in CCP discharge with DC voltages at -10 V, -20 V and -50 V are shown Fig. 7(a), Fig. 7(b) and Fig. 7(c), respectively. Formation of CNTs was confirmed for DC bias of -10 V to the Si substrate. The CNTs were multi walled CNTs with their average diameter of 50 nm and height of several μm. As DC voltage more negative than -10 V was applied, CNTs growth was not confirmed, but carbon nanowalls (CNWs) with wall thickness of 50 nm and height of several μm were observed.

Carbon films prepared with DC voltages of -50 V, -100 V and -200 V applied to the Si substrate in ICP discharges are shown in Fig. 7(d), Fig. 7(e) and Fig. 7(f), respectively. Contrary to the CCP case, CNTs growth was not confirmed for bias voltages more positive than -200 V, carbon nanowalls with wall thickness of 50 nm and height of several μm were formed. Well aligned CNTs were produced as DC voltage more negative than -200 V was applied. Conditions for CNTs growth for both types of discharges are summarized in Table. 1.

Table.1. CNT growth parameter of both RF discharges.

	CCP	ICP
Ni Sputtering		
Pressure	Ar 4 Pa	Ar 1Pa
DC bias	None	-200 V
Material	Ni sheet	Ni wire
Time	5 min	5 min
RF power	100 W	100 W
CVD process		
Pressure	CH_4 5 Pa ; H_2 3 Pa	CH_4 4 Pa ; H_2 1 Pa
DC bias	-10 V	-200 V
Temperature	823 K	823 K
Time	10 min	10 min
RF power	200 W	200 W

Regarding to the effect of bias voltage applied to the substrate, Yen *et al.* [9] have reported that any bias voltage more negative than 0 V realized the growth of CNTs in their ICP system. Our experimental results requiring bias more negative than -200 V for CNTs growth are probably due to the difference from their experiment in plasma excitation structure and the corresponding plasma parameters.

4. Conclusions

In our research, difference of CCP discharge and ICP discharge was compared by Langmuir probe and OES measurements. By probe measurement, the electron temperature of CCP was measured to be higher than that of ICP near the center of substrate. The radial distributions of electron temperature showed a characteristic contrast from CCP to ICP. The radial distribution of CCP gradually decreased to the edge, while that of ICP increased toward the edge. The electron density in ICP was substantially higher than that of CCP. Electron density of CCP was appreciably small in the area other than the vicinity of magnetron area.

By OES measurement, radical species and intensity ratios in the plasma were measured to be similar in both CCP and ICP. Both CCP and ICP plasmas produced aligned CNTs, but negative bias voltages suitable for CNTs growth were different. In our discharge configuration, CCP plasma had required bias voltage about -10 V for CNT growth, while -200 V realized a CNTs growth in ICP plasma conditions.

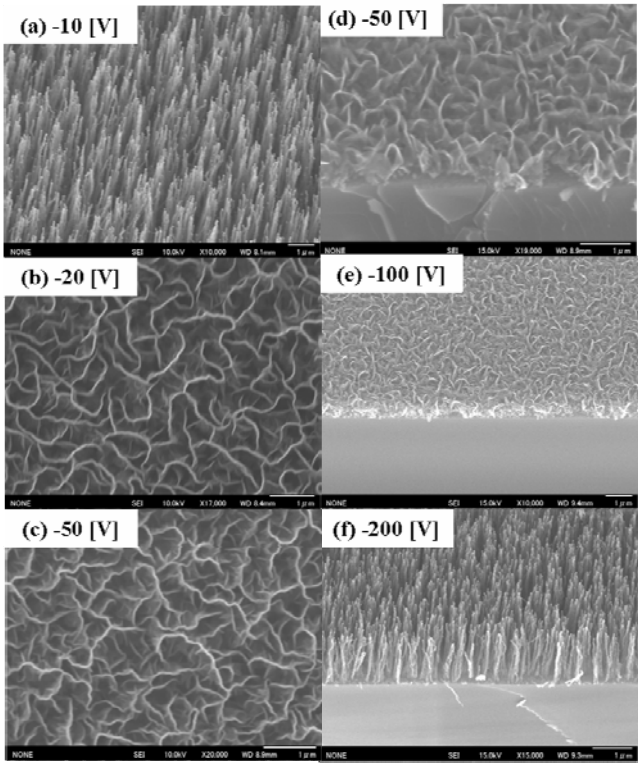

Fig.7. SEM images of carbon nanostructure by varying negative bias voltage using CCP and ICP. (a)-(c) CCP discharges, (d)-(f) ICP discharges.

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