

A Dual-RF-Plasma Approach for Controlling the Graphitic Order and Diameters of Vertically-Aligned Multiwall Carbon Nanotubes

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ABSTRACT

Plasma enhanced chemical vapor deposition (PECVD) is a unique technique for growing vertically-aligned multiwall carbon nanotubes (VA-MWNTs) at controllable tube densities. This technique is of considerable importance for low temperature growth of VA-MWNTs at desired locations. However, the graphitic order of these MWNTs is inferior to those grown by laser ablation, arc discharge, and thermal CVD techniques. Previously, these VA-MWNTs were grown by a one-plasma approach (DC, microwave etc), either for gas decomposition or substrate biasing. Here, we describe a dual-RF plasma enhanced CVD (dual-RF-PECVD) technique that offers unique capability for controlling the graphitic order and diameters of VA-MWNTs.

INTRODUCTION

Carbon nanotubes (CNTs) are among the promising materials that are expected to play a major role in future nanoscience and nanotechnology. Their unique structural and electronic properties make them a potential candidate for many nano-electronic, mechanical, chemical, and biological applications. Some applications require CNTs to be grown with controllable dimensions and growth orientation. For example, electron field emission devices demand that the growth of CNTs be vertical-aligned to the substrate surface. Plasma enhanced chemical vapor deposition (PECVD) is of considerable importance for low temperature growth of VA-MWNTs at desired locations. However, the graphitic order of these MWNTs is inferior to those grown by laser ablation, arc discharge, and thermal CVD techniques. VA-MWNTs grown by PE-CVD are usually called carbon nanofibers (CNFs) and have highly distorted structures. Previously, these CNFs were grown by a one-plasma approach, either for gas decomposition or substrate biasing [1-4]. Here, we describe a dual-RF-plasma enhanced CVD (dual-RF-PECVD) technique that offers unique capability for controlling the graphitic order and diameters of VA-MWNTs.

By the dual-RF-PECVD, we have demonstrated the growth of VA-MWNTs to an area as large as 25 cm² at a substrate temperature as low as 540 °C [5]. The use of two RF-power sources in the technique allowed independent control of the potential and kinetic energies of the growth species. The potential energy refers to the excitation and ionization rates of the growth species. The kinetic energy depends on the speed of the ionic species accelerated toward the substrate by the substrate negative bias voltages. Here, we describe the function of these plasmas on the graphitic order and diameters of VA-MWNTs.

EXPERIMENTAL DETAILS

Two radio-frequency (RF) plasmas are used for the growth of VA-MWNTs. The dual-RF-PECVD chamber is shown in figure 1a. The plasma produced on the top electrode (figure 1b) is referred as the top plasma, whereas the plasma produced on the bottom electrode and substrate is referred as the bottom plasma. The spacing between the two electrodes is maintained at 5 cm. The substrate is about 3.5 cm from the top electrode and 1.5 cm from the bottom electrode. The top plasma is adjusted according to the forward RF power from a power generator. Another power generator controls the bottom plasma by adjusting the bias voltage resulting on the substrates. In this manner, the top plasma can be used to control the potential energy of the growth species, as it is responsible for the ionization of the hydrocarbon gas. The bottom plasma is used to control the kinetic energy of the growth species. The potential difference generated on the substrate will accelerate the ionic species to bombard the growth surface and assist the growth of VA-MWNTs. In this experimental setup, the substrate is placed on a BN ceramic heater, which is in contact with the bottom electrode. This heater controls the growth temperature by using a thermal-couple and a proportional-integration-differentiation (PID) controller.

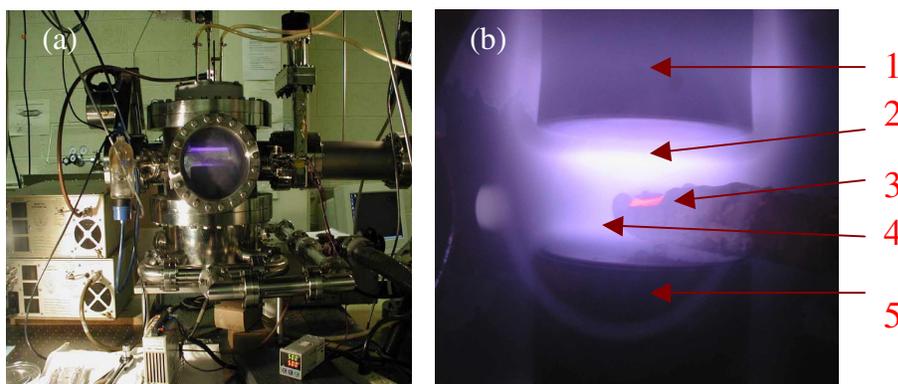


Figure 1. (a) Experimental setup of the dual RF-PECVD chamber. (b) Magnified view of (1) top electrode (2) top plasma (3) heater (with substrate) (4) bottom plasma (5) bottom electrode

For all experiments discussed in this paper, Ni is used as the catalyst that initiates the growth of MWNTs. These catalysts are in the form of nanoparticles, which are generated by heat treatment of Ni thin films at 600 °C before the growth of MWNTs. These Ni films are deposited by pulsed laser deposition on Si substrates that have a layer of SiO₂ film (~500 nm thick). This SiO₂ film serves as the diffusion barrier that prevents interaction of between the Ni films and the Si substrates. Pure methane gas (CH₄, 99.9%) is used for the growth of the MWNTs at a pressure of 0.2 mTorr. A flow rate of 350 sccm is maintained during the growth of MWNTs. In order to investigate the effect of the RF-plasma on the growth of MWNTs, we have kept other growth parameters constant. The growth temperature is maintained at 600 °C and the Ni catalyst films thickness are about 7 nm for all cases. We purposely chose this thickness for the catalyst films so that MWNTs with thick diameters (>100 nm) will be grown. This will demonstrate clear changes in the diameters of MWNTs with the changes of plasma parameters.

DISCUSSION

We found that both the top and the bottom plasma have their influence on the diameters and graphitic order of VA-MWNTs:

Effect of Top Plasma Forward Power on the Diameters of VA-MWNTs

We have investigated the effect of the top plasma forward power on the growth of MWNTs. The forward power to the top plasma is changed while keeping the substrate biasing at -150 V. We have studied cases with a forward power ranging from 50 W to 200 W in 50 W increments. The results from these experiments are shown in the SEM images in Figure 2. As shown, it is observed that with an increase in forward power, the diameters of the MWNTs increased accordingly. The increase of the forward power will cause the increase of both the kinetic energy and ionic flux in the top plasma. This results in the increase of electron temperatures inside the plasma. Plasma heating occurred and increases the surface energy of the Ni nanoparticles. These particles will form larger clusters to minimize the surface free energy for stabilization. Thus, the diameter of the nanoparticles and nanotubes were increased. In general it is observed that the size of the nickel nanoparticle dictates the diameter of the MWCNTs.

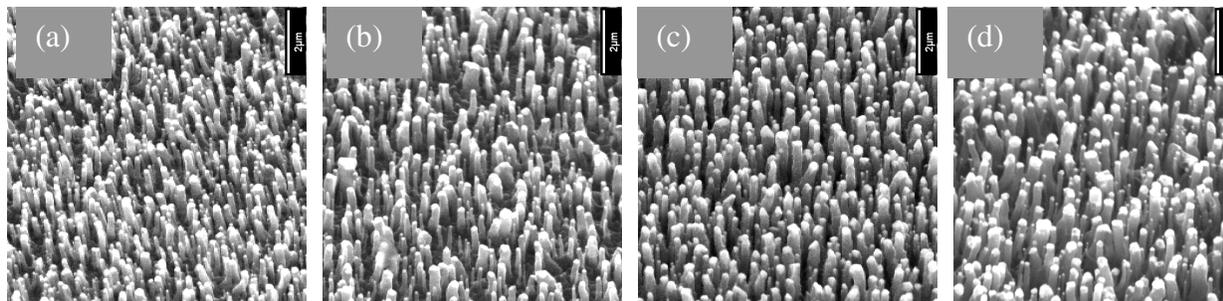


Figure 2. SEM images of VA-MWNTs grown at different top plasma forward powers (a) 50 W, (b) 100 W, (c) 150 W, (d) 200 W. Other growth parameters remained constant.

Effect of Bottom Plasma on the Diameters of VA-MWNTs

We have also investigated the effect of bottom plasma by varying the negative dc substrate bias voltage while keeping the top plasma forward power at 200 W. For these series of experiments, the growth temperature is kept constant at 600 °C. The substrate biasing is varied from -50 to -200 V in increments of 50 V.

An interesting trend is observed with the changing of negative bias voltage. Initially, an increase of tube diameters is observed when the biasing varied from -50V to -150V. The increase of substrate biasing enhanced the kinetic energy of the impinging ions. The ionic flux near the substrate region also increases with the increase of the bottom plasma reactivity. Thus the energy transfer to the substrate surface will be enhanced through ion bombardment. This will increase the surface energy of the Ni nanoparticles. To minimize the surface energy, the nanoparticles form large clusters for stabilization. Thus the diameters of the nanotubes increased. In fact ion

bombardments will cause heating of the substrates. However, due to the use of PID temperature controller, the substrate temperature will remain constant after compensating the electrical power to the heater [4].

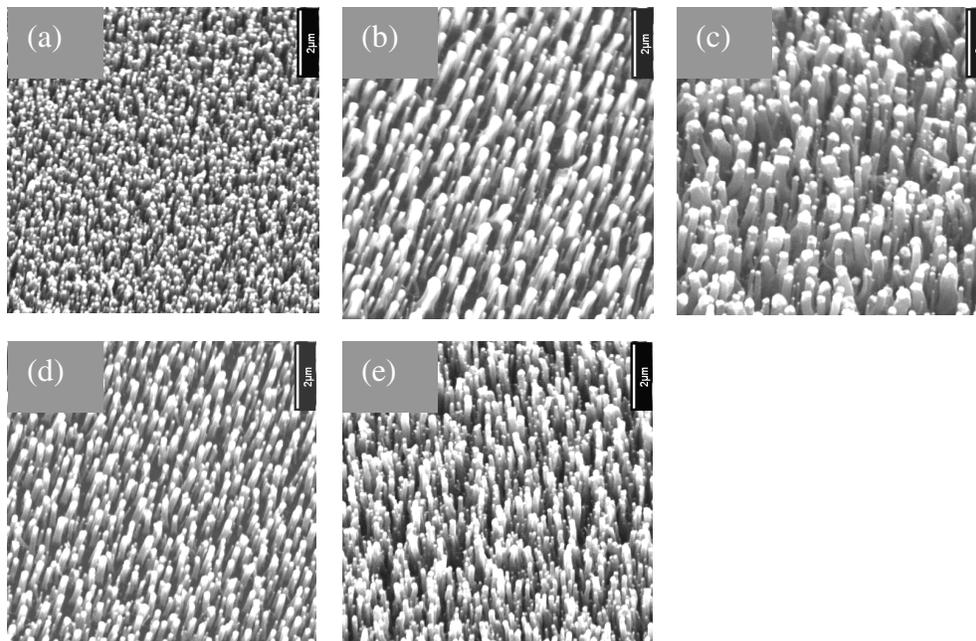


Figure 3. SEM images of VA-MWNTs grown at different substrate bias voltages as controlled by the bottom plasma (a) -50 V, (b) -100 V, (c) -150 V, (d) -200 V, and (e) -250 V. Other growth parameters remained constant.

However, when the bias voltage reaches a level between -150 and -200 V (figure 3c to 3d), a sudden decrease in diameters of the MWNTs is detected. This can be explained by the sputtering of Ni nanoparticles by the energetic ions. The diameters continue to decrease at a biasing of -250 V (figure 3e). No MWNTs were formed when the biasing is higher than -350 V, which is the total re-sputtering region.

Effect of Top and Bottom Plasmas on the graphitic order of VA-MWNTs

We use Raman spectroscopy to scrutinize the effects of plasma parameters on the graphitic order of these VA-MWNTs. This is possible by comparing the intensity of the graphitic (G) and disordered (D) Raman bands, representing zone center phonons of E_{2g} symmetry and K -point phonons of A_{1g} symmetry, respectively. The intensity ratio of these two bands (I_G/I_D) is commonly used as a measure of graphitic order of carbon-based materials. All measurements are carried out by a confocal micro-Raman system, using a HeNe excitation laser ($\lambda = 632.8$ nm), with an average laser power of ~ 50 mW. The probed area on the sample is $\sim 2 \mu\text{m}^2$. Each spectrum is an average of five measurements taken at different areas of the sample. The integration time for each measurement is 10 sec.

From the Raman spectra in figure 4a, it is evident that the graphitic order increase with the increase of top plasma forward power from 50 W to 200 W at constant dc bias of -150 V. The relation of I_G/I_D to the forward power is shown in figure 4b. As shown, there is a tendency that the I_G/I_D ratio increases at a forward power of 200 W. This result indicates that the graphitic order of MWNTs is enhanced with the increase of forward power to the top plasma.

On the other hand, figure 4c shows the Raman spectra for VA-MWNTs grown by 200 W of top plasma forward power at various substrate biasing. The corresponding relation of I_G/I_D to the substrate biasing is shown in figure 4d. As shown, the I_G/I_D ratio is low at low substrate biasing (-50 V) but is increased to I_G/I_D of ~ 0.8 at higher substrate biasing. This result indicates that a biasing threshold occurred for the growth of MWNTs with high graphitic order. These are consistent with TEM images obtained. Details of these results will be discussed elsewhere.

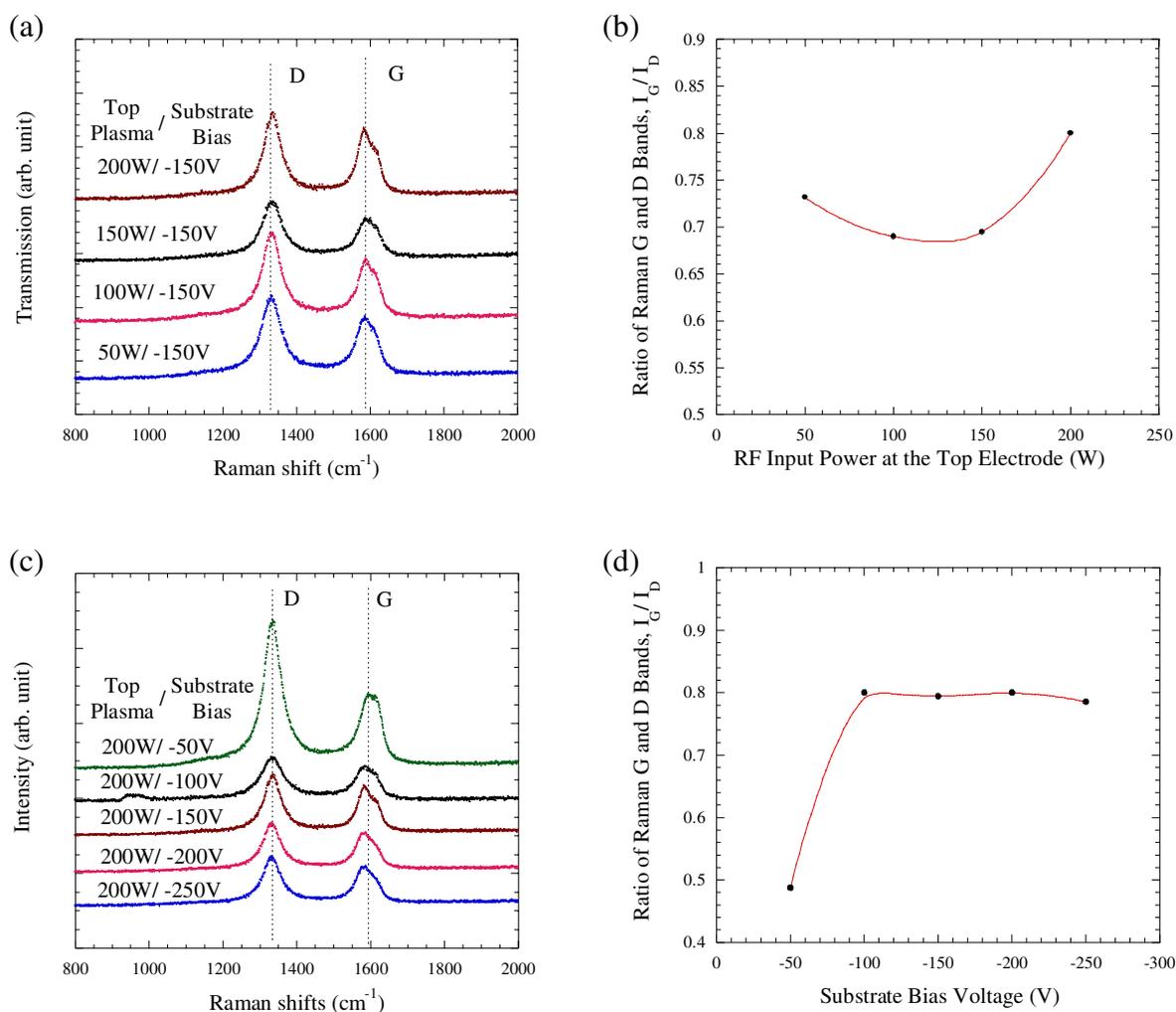


Figure 4. (a) Raman spectra for VA-MWNTs grown at various top plasma forward power and (b) the corresponding I_G/I_D relation. (c) Raman spectra for VA-MWNTs grown at various substrate biasing and (d) the corresponding I_G/I_D relation.

CONCLUSIONS

In summary, the diameters and graphitic order of VA-MWNTs can be effectively controlled by the dual-RF-PECVD technique. This is accomplished by adjusting either the forward power to the top plasma or the negative dc bias voltages on the substrates.

ACKNOWLEDGEMENTS

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List of revisions:

This manuscript has been revised according to the suggestions:

1) In the last paragraph at page 1, we explain the potential and kinetic energies of the growth species by replacing the original statement by the following sentences:

The use of two RF-power sources in the technique allowed independent control of the potential and kinetic energies of the growth species. The potential energy refers to the excitation and ionization rates of the growth species. The kinetic energy depends on the speed of the ionic species accelerated toward the substrate by the substrate negative bias voltages.

2) We have corrected the repeating subtitle as

Effect of Bottom Plasma on the Diameters of VA-MWNTs

3) We have corrected Fig 4 d. with a smooth fitting curve.

4) English of the manuscript has been corrected as suggested. We made one addition correction in the abstract:

From

“This technique is considerably important for low temperature”

To

“This technique is of considerable importance for low temperature”

Similar correction was done in the first paragraph of the introduction:

From

“Plasma enhanced chemical vapor deposition (PECVD) is considerably important for..”

To

“Plasma enhanced chemical vapor deposition (PECVD) is of considerable importance for..”