Vacuum 84 (2010) 1398–1401

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

# Structure modifications of vertically grown carbon nanotubes by plasma ion bombardment

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A R T I C L E I N F O

*Article history:*
Received 3 July 2009
Received in revised form
14 December 2009
Accepted 5 January 2010

*Keywords:*
Carbon nanotubes
Structure modification
Plasma ion bombardment
DC plasma
Height reduction

A B S T R A C T

We report the structural modifications of vertically grown carbon nanotubes (VCNT) by plasma ion bombardments. The VCNT were grown by thermal chemical vapor deposition (CVD) using acetylene feedstock with iron catalyst and alumina supporting layers on silicon substrate. The plasma ion bombardments were performed using DC plasma enhanced CVD with parallel electrodes configuration. As a result, the height of the as-grown VCNT decreased with increasing applied bias voltages, plasma powers and working pressures. In addition, we observed the aggregated morphologies of the VCNT top surface after the plasma treatments which would be useful for field emission display and energy storage applications.



## 1. Introduction

Carbon nanotubes (CNT) are made by rolling of graphite sheet [1] and thus have one dimensional structure with ultrahigh aspect ratio in nanometer ranges. These peculiar nanostructures broaden their potential application as field emitters [2]. In order to facilitate the application, lots of post-treatments have been actively studied to enhance the field emission ability with prolonged emission stability by using various post-treatments [3–8]. Especially, plasma aided post-treatment have been widely used because it is possible to control the energy and dose of the energetic species by adjusting the plasma parameters. Most of the works to date have observed the formation of aggregated CNT tip and focused only on the change of field emission properties after the treatments. However, lack of systematic investigation from a viewpoint of plasma process was a barrier to maximize their potential since we can trim more precisely and optimize the CNT morphology which contributes to the enhancement of field emission properties by careful plasma parameter control.

Here, we demonstrate the structure modification of vertically grown CNT (VCNT) using plasma ion bombardment techniques with a systematic way. Firstly, we grew vertically aligned CNT using thermal chemical vapor deposition (CVD). Then, Ar DC plasma was mainly utilized to perform the ion bombardments. We mainly changed the substrate bias voltages and working pressures in order to control the ion energies and flux of the plasmas. Further, we investigated the effects of plasma gases on the final VCNT structures and briefly discussed the mechanism of plasma aided CNT structure modification observed.

## 2. Experimental

In order to grow VCNT, an aluminum oxide buffer layer (10-nm $Al_2O_3$) and catalyst (1-nm Fe) film were subsequently deposited by electron beam evaporation method. The deposited substrates were inserted into a quartz furnace [Fig. 1(a)]. A mixture of acetylene, argon, and hydrogen was used to grow the VCNT at atmospheric pressure. The detail of the growth process is described elsewhere [9]. Plasma ion bombardment was performed using a DC plasma enhanced CVD unit [Fig. 1(b)] with Ar or $H_2$ process gas.

For structure observation and height estimation of the VCNT, scanning electron microscope (SEM) was used. Surface morphology was probed using atomic force microscope (AFM) in a tapping mode. Raman spectroscopy was useful for a quantitative analysis of structure modifications through intensity ratio ($I_D/I_G$) changes between defect-induced (D) band and graphite (G) band.

## 3. Results and discussion

Fig. 2 presents representative SEM images showing the structural differences between as-grown VCNT and Ar plasma treated

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doi:10.1016/j.vacuum.2010.01.007

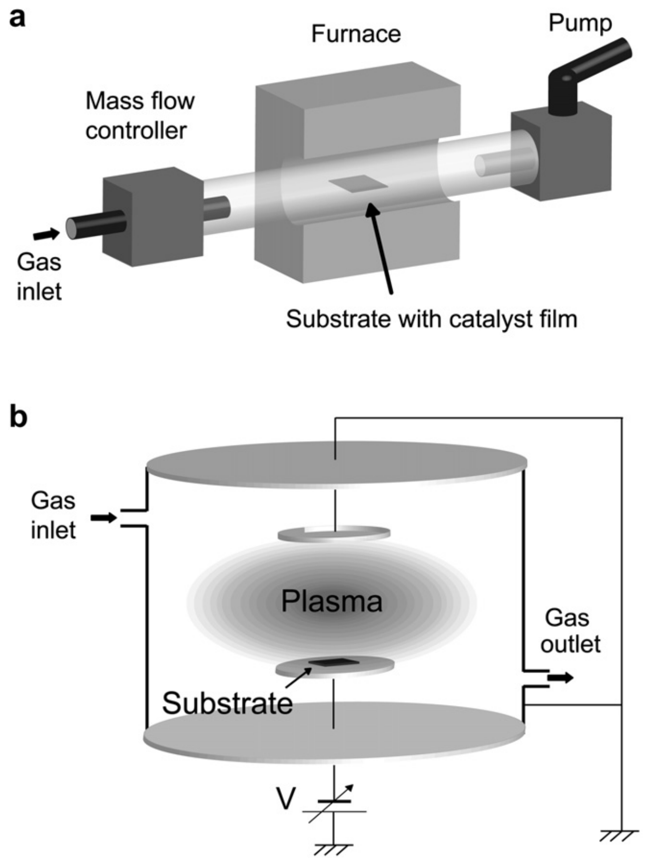


**Fig. 1.** (a) Thermal CVD unit for VCNT growth. (b) Plasma CVD unit for plasma ion bombardment.

VCNT. It is found that a significant height reduction of the VCNT occurred by plasma ion bombardment. For example, the as-grown VCNT [Fig. 2(a)] had 640 μm in length and reduced to 550 μm [Fig. 2(d)] after the Ar plasma ion bombardment with 300 V for 10 min at 0.7 Torr. Fig. 2(b) and (e) clearly show the difference of top surface structures before and after the plasma treatment.

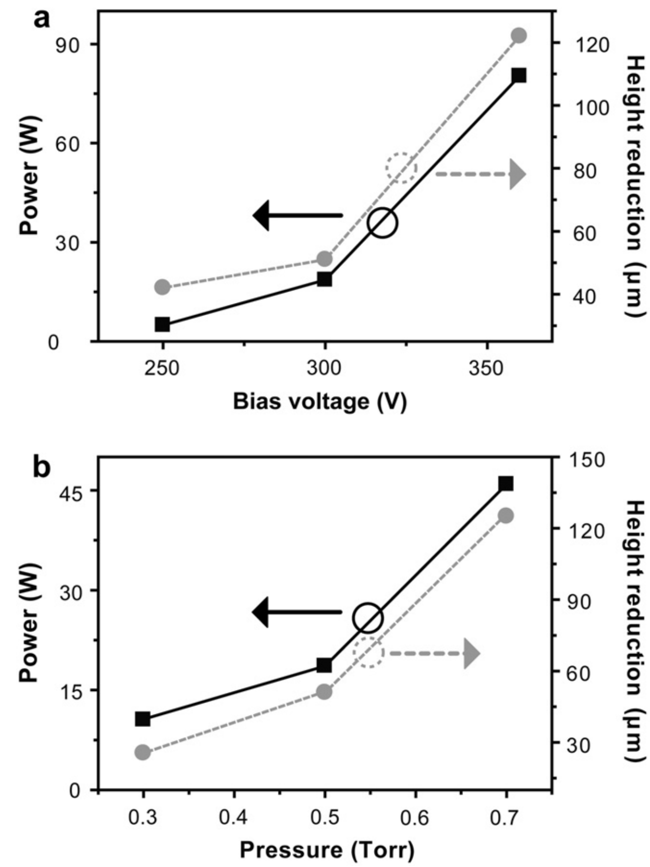


**Fig. 3.** Effects of (a) applied bias voltages and (b) working pressures on plasma power and VCNT height reduction. Plasma pressure in Fig. 3(a) was 0.5 Torr and applied bias voltage in Fig. 3(b) was 300 V.

As-grown VCNT has uniform surface structures with partially entangled tube-ends as shown in high magnified image [Fig. 2(c)]. On the other hand, the structure of top surface was modified after the Ar plasma ion irradiation by making cone-shaped tip structures as shown in [Fig. 2(e)]. The density of the aggregated structures

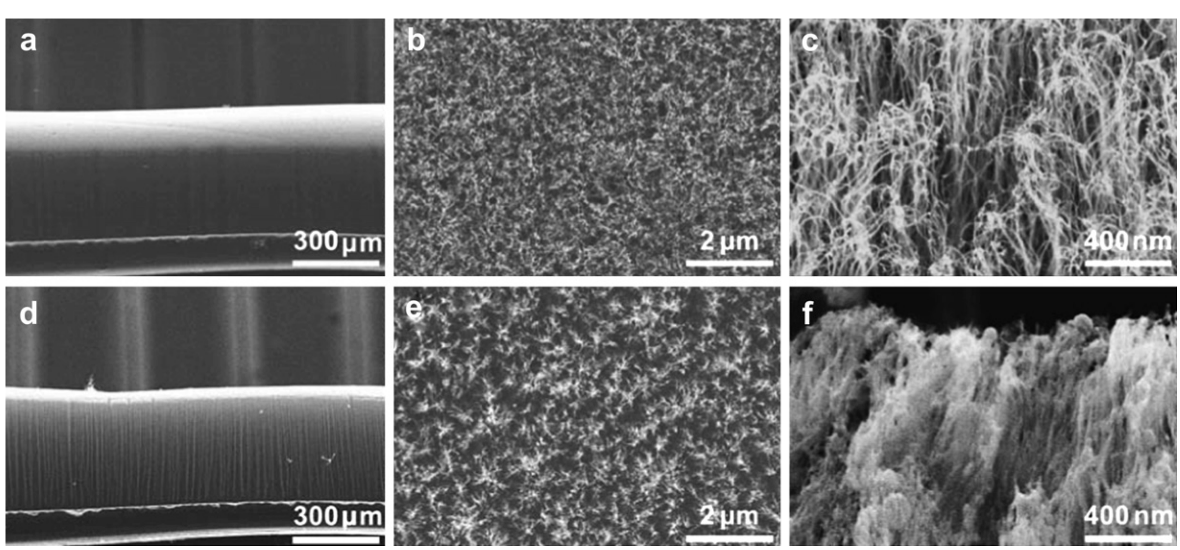


**Fig. 2.** SEM images showing the structural differences between (a–c) as-grown VCNT and (d–f) Ar plasma treated VCNT. (a) and (d): Cross sectional view. (b) and (e): Top view. (c) and (f): Magnified tilt images showing the different tip structures.