Effects of Electric Field on the Growth of One-dimensional Carbon Materials in the Chemical Vapor Deposition Process

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ABSTRACT

In this study, Si wafer coated with sputtered $Fe_{0.8}Co_{0.2}$ alloy was adopted as the substrate which was placed in a tube furnace for the growth of Carbon NanoTubes (CNTs) and Carbon nanofibers (CNFs). Methane mixed with hydrogen and argon was used as gaseous precursor for carbon deposition. In order to obtain aligned array of carbon nanotubes, an electric filed was applied on the wafer. Effects of pressure, gap distance of the electrode, applied voltage, concentration and flow rate of the reactant, and deposition period on the growth of the aligned carbon nanotubes and fibers were investigated. Moreover, the field emitting properties of the as-fabricated CNTs and CNFs were measured and the morphologies were examined.

Keywords: carbon nanotubes, chemical vapor deposition, field emission property, CVD

1 INTRODUCTION

Since the discovery of carbon nanotubes in 1991[1], lots of studies on the physical and the chemical properties were reported. Numerous potential applications such as hydrogen and Li-ion storage, flat panel displays, chemical sensors, SPM probe tip, and composites etc. were proposed[2-5]. Mass production with high quality CNTs is a prerequisite for these applications. On the synthesis of CNTs, three primary routes, including arc-discharge, laser ablation, and chemical vapor deposition (CVD), were proposed. Each method has its peculiarity, for example, CNTs made from the arc-discharge process accompanied with the formation of a great amount of amorphous carbon particles, and the laser ablation process have great opportunity to produce single wall carbon nanotubes (SWCNTs) and carbon nanohorns; on the other hand, the CVD process is a promising method for mass production of carbon nanotubes.

Once CNTs were adopted for the application of field emission display, it requires that the CNTs have to be dispersed uniformly on the cathode. Two routes are available for that purpose. One is screen printing of slurry (mixtures of CNTs, conducting material, and solvent) on the cathode, however, uniformity of CNT dispersion could be a problem. The other method is the growth of CNTs on the cathode directly. It believes that the emitting properties can be enhanced if CNTs are aligned vertically. Various CVD methods have been used in order to achieve this purpose. Fe-deposited porous Si substrates were used and pyrolysis of acetylene was adopted as carbon precursor, field emission current density 80 mA/cm^2 with field (3V/mm) was reported [6]. In order to obtain well-aligned CNTs, CVD process with or without bias-enhanced microwave plasma was adopted and vertically aligned CNTs on substrate were reported [7,8]. Besides, it is reported that well aligned MWNTs can be obtained by positively biasing the substrate during the growth[9]. In this work, the effects of bias voltage on the growth of CNTs in a tube furnace during CVD growth have been investigated.

2 EXPERIMENTAL

2.1 Substrate preparation

Silicone(100) wafers coated with different thickness (100, 50, and 10 nm) of $Fe_{0.8}Co_{0.2}$ layers by sputtering was adopted as substrate. Heat treatment was applied before deposition under the atmosphere of mixtures (90% argon + 10% hydrogen); as a result, different sizes of catalyst island can be obtained.

2.2 Deposition parameters

The wafers were annealed at 450℃ in 10^{-2} torr for 5 minutes, and then buffer gas of Ar/H^2 was channeled into chamber with a flow rate of 30 sccm; at the same time, the chamber temperature was increased up to reaction temperature under an increase rate of 8℃/min. The pressure of the chamber was kept at 500 torr during deposition, and a steady flow was maintained in chamber by letting argon pass through a benzene container which was kept at 40℃.

2.3 Apparatus for dc bias and field emission properties tests

The catalyst-coated substrate was placed within two Mo electrodes separated at a distance of 1 mm or 06 mm. Positive or negative dc bias of 50 to 120 V were applied to the electrode. Field emission properties were tested in a high vacuum chamber which was evacuated down to a pressure lower than 10^{-6} mbar. Space between the electrodes was kept at 100μm.

2.4 Microstructure Examination

Field Emission scanning electron microscope (FESEM, JEOL JSM-6500F) and Transmission electron microscope (JEOL 200cx) were used to examine the nanotube alignment and microstructure.

3 RESULTS AND DISCUSSION

3.1 Nanotube growth without bias voltage

In this process, the flow rate of 30 sccm and reaction temperature of 900 ℃ were used. The deposition period is 10 minutes. Figure 1 shows the FESEM of the synthesized CNTs (denoted as Sample 1) under the flow rate of 45 sccm. Figure 2 shows the hollow structure of the tube. Figure 3 depicts the field emission current density versus electric field. The turn-on voltage of 3.8 V/μm with a current density of 0.5 mA/cm^2 can be obtained. It is also observed that turn-on voltage decreases with the increase of methane flow rate, and current density is proportional to the CNT density.

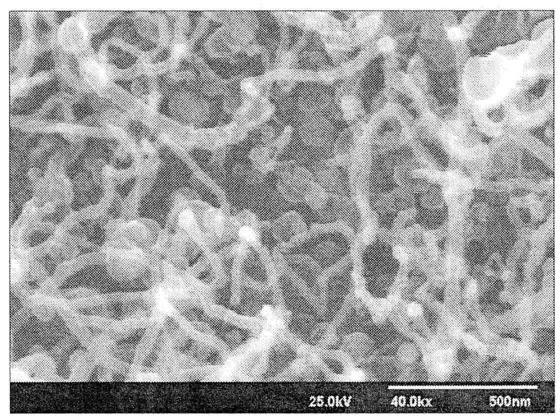

Figure 1 FEGSEM image of as-synthesized CNTs.

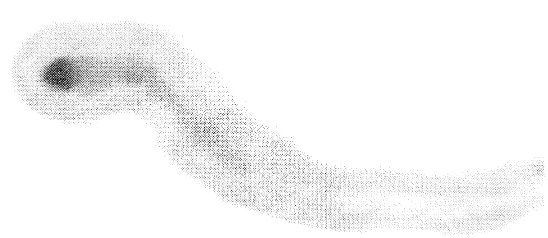

Figure 2 Hollow structure with catalyst located at the tip of the carbon nanotube.

3.2 Nanotubes growth with bias voltage

In order to obtain vertically aligned CNTs, a positive or negative dc bias of 50 V were applied. In the case when the bias is not high enough or the gap between electrodes is too large, randomly oriented CNTs were observed. At some specific experimental conditions, arc on the anode, produced by the fastest growth CNT, was detected. Different dc bias (positive or negative) also affected CNT growth. If negative dc bias was adopted, larger gap between electrodes have to be used to avoid arc. Figure 4 showed CNTs synthesized under 300 torr for 10 minutes by using positive dc bias with a 0.6 mm gap (denoted as Sample 2). As compared with Sample 1 CNTs as shown in Figure 1, Figure 4 depicts a better alignment although no perfectly vertical CNTs was found in this figure.

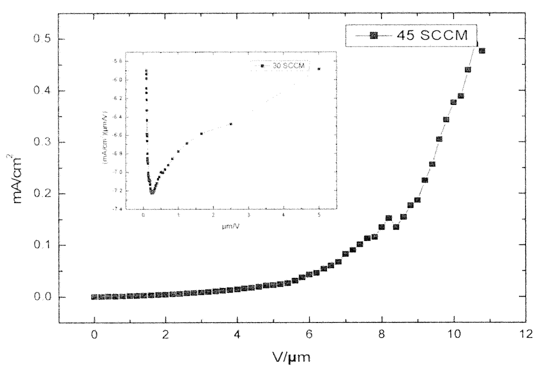

Figure 3 Field emission current density versus electric field for Sample 1.

Once the positive dc bias was replaced by the negative bias, the alignment is further improved; as shown in Figure 5, all the CNTs, denoted as Sample 3, grew upward and a head containing catalyst at the tip was observed. Formation of the head with bigger size than tube is probable due to the rapid adsorption of carbon atoms on the charged tip.

On the field emission property test, Figure 6 shows a current density of 0.18 mA/cm^2 with the turn-on voltage of 3.4 V/μm for Sample 3.

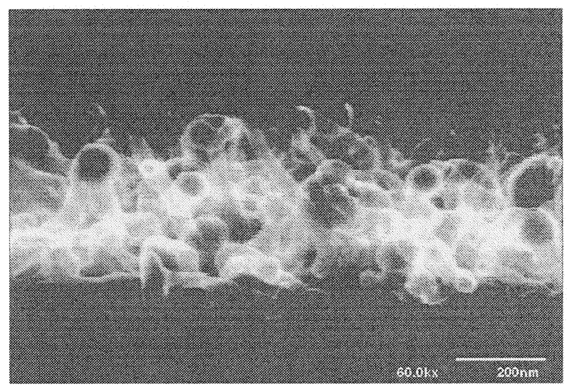

Figure 4 CNTs synthesized in a pressure of 300 torr under a positive dc bias (Sample 2).

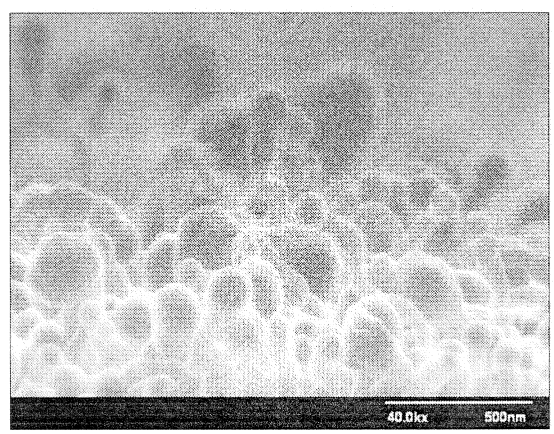

Figure 5 Vertical CNTs synthesized under a negative dc bias (Sample 3).

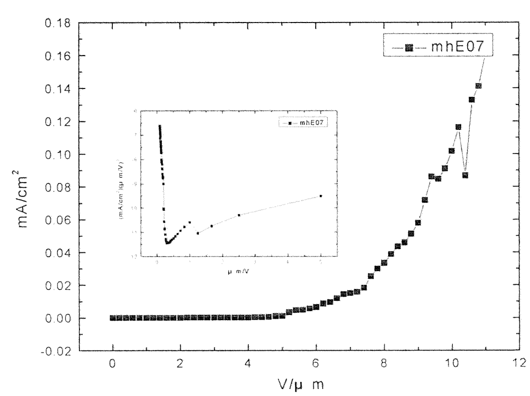

Figure 6 Field emission current density versus electric field for Sample 3.

In order to study the effects of bias on CNT growth, a higher bias of 120 V was applied, on the other hand, the gap between electrodes was also increased. Thus, the electric field enhanced from 50 V/mm to 60 V/mm. The advantage for such adjustment can not only increase the electric field but also enhance the precursor concentration between the electrodes. The CNTs synthesized under the conditions were denoted as Sample 4

Field emission properties of Sample 4 were shown in Figure 7. It depicts a current density of 3.0 mA/cm^2 with the turn-on voltage of 3.03 V/μm. Based upon the microstructure of the synthesized products, the one-dimensional products on the substrate could be the CNFs in stead of CNTs. Better performance in field emission property of Sample 4 is probably due to numerous carbon nodes deposited on the surface of carbon nanofibers.

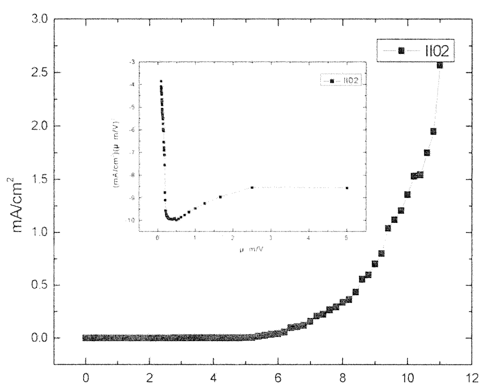

Figure 7 Field emission current density versus electric field for Sample 4.

4. CONCLUSIONS

In this work, the growth of one-dimensional carbon material is obtained by applying bias voltage between the electrodes, even the bias is as low as 60 V/mm. The emission current density obtained was 3.0 mA/cm^2 under an electric field of 3.03 V/μm. This study also finds that the status of bias (positive or negative) also plays an important role on the fabrication of vertically aligned carbon nanotubes and nanofibers.

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