Field emission characteristics of carbon nanofibers grown on the electroplated copper micro-tips

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Abstract

Carbon nanofibers (CNFs) were synthesized on copper micro-tips by using direct current plasma enhanced chemical vapor deposition using C_2H_2 and NH_3 gas at 480℃. Nickel catalyst was used to grow CNFs, which was formed on copper micro-tips by high current electroplating. The turn-on voltage of the CNFs was about 2.9 V/㎛ with an emission current density of 10 ㎂/cm^2, and the maximum emission current density of 2.46 mA/cm^2 was observed over the area of 0.2827cm^2, at the electric field of 4.59 V/㎛. The CNFs formed by the present method have clear advantages for the application of the emitters of FEDs and a large area vacuum lighting source because of the low growing temperature and low turn-on field.

***Keywords*: field emission, CNFs, CNTs, electroplating, PECVD**

Introduction

Carbon nanotubes (CNTs) [1] have recently emerged as an attractive cold cathode material due to their excellent field emission characteristics such as low turn-on field, high current density, and long-term stability. Interestingly, another form of carbon nanostructures, such as carbon nanofibers (CNFs) [2], has also demonstrated their comparably excellent electron emission behavior. CNTs and CNFs are suitable, in particular, for high current-density applications under vacuum conditions due to their high physical and chemical stability, and high electrical and thermal conductivity.

Chemical vapor deposition (CVD) has been widely used for the synthesis of various carbon nanomaterials. It is well known that the catalyst plays an important role in growing CNFs by using CVD method. Chemical composition and particle size of the catalyst determine the structures, properties and dimensions of the CNFs. Various methods have been developed to prepare the catalyst for synthesizing CNFs. Merkulov et al. [3] evaporated Ni on n-type Silicon by e-gun. Shyu and Hong [4] deposited Fe-Ni with various components by e-beam evaporation. Some groups have reported the synthesis of CNFs using electroplated catalysts. [5, 6, 7, 8, 9]

CNFs grown on various surface morphologies of substrates have been reported to obtain the emitters with high preformance, such as silicon nanowires formed by high temperature thermal CVD [10], tungsten tip [11], and etc. However, the surface morphologies mentioned above require complicated processes such as high temperature thermal pyrolysis [10] or wet etching [11]. In this paper, we report the synthesis of CNFs on copper micro-tips formed by easy and

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simple electroplating method and their field emission characteristics.

Experiment

Before forming the copper micro-tips by electroplating, 30-nm-thick Cr and 300-nm-thick Cu layers were deposited on glass or silicon substrate sequentially by thermal-vacuum evaporation. The Cr layer located between the Cu electrode and the silicon substrate works as an adhesion layer. To form the copper micro-tips by electroplating, sulfuric acid-copper sulfate chemical solution was used in the present study , which contain 75 g/l of $CuSO_4{\cdot}5H_2O$, 180 g/l of H_2SO_4, 70 mg/l of HCl. Pulse plating with a peak current of 850 mA, duty ratio of 60%, and frequency of 1000 Hz were employed. A copper electrode layer with the area of 4 cm^2 (2 cm × 2 cm) was used as the cathode and a copper plate containing phosphorus was used as the anode in the electroplating.

The copper micro-tips were uniformly formed by high current electroplating and then, they were coated with 30-nm-thick Ti and 20-nm-thick Cu film for the buffer layer and electrode layer, respectively. Ni electroplating was followed on the copper micro-tips which were coated by Ti and Cu layer. Ni worked as a catalyst to grow CNFs. Nickel sulfate ($NiSO_4{\cdot}6H_2O$), nickel chloride ($NiCl_2{\cdot}6H_2O$), boric acid (H_3BO_3) were used as electrolytes for a dc electroplating process. The temperature and pH of the electroplating bath were 23℃ and 3.7, respectively. The electroplating current density was 10 mA/cm^2.

The samples were transferred to the growing chamber. Then the chamber was evacuated by a mechanical pump and the substrates were heated up to 480℃. For plasma deposition, a dc discharge between the heater stage (cathode) and the gas shower head (anode, 2.5 cm above the stage) was ignited by applying a fixed voltage of 450 V. C_2H_2 was introduced via a separate mass flow controller. The ratio of C_2H_2: NH_3 was kept constant (25 sccm : 50 sccm) under a total pressure of 8 torr. A stable discharge current of 100 mA was maintained for a whole deposition process time of 30 min. The temperature was measured using a thermocouple directly mounted on substrate.

Field-emission characteristics of CNFs were investigated by using a diode-type configuration, a cathode, and a parallel anode plate in a vacuum chamber maintained at a pressure of 4×10^{-7} torr with an oil-free turbo-molecular pump. To prevent abrupt breakdown, the cathode was earth-grounded by using a 2MΩ ballast resistor. The specimen with CNFs and an indium-tin oxide (ITO) glass were used as the cathode and the anode, respectively, and 610-㎛-thick spacer was located between the anode and the cathode. The emission current was evaluated by averaging the measured current over the area of a hole with the diameter of 6 mm in the spacer through which the current was collected. The specimen was aged enough to remove contaminants and to degas before the measurement. Voltage with a sweep step of 20 V was applied between the anode and the cathode to extract the electrons out of the CNFs. A Keithley 248 high voltage supply was used for the power source and a Keithley 2000 multimeter was used to measure the current. The field-emission measurements were performed several times for the sample and recorded using a computer with data acquisition software.

Results and Discussion

Figure 1 (a) shows scanning electron microscope (SEM) images of copper micro-tips formed by electroplating. The copper micro-tips are uniformly distributed and have vertically aligned corn shape with tips' diameters ranging from 30 to 50 nm and the length is about 10 ㎛. Figure 1 (b) shows SEM images of Ni catalysts formed on copper micro-tips by electroplating method. Ni catalysts have the rough surface which helps reaction with feeding gases. Figure 2 shows SEM images of the CNFs. The figure shows that some of the CNFs are vertically aligned while others are curved or bent. The CNFs have branch of protrusions. The CNFs were

300~500 nm in diameter and 20 μm in length, and the protrusions were 10~20 nm in diameter.

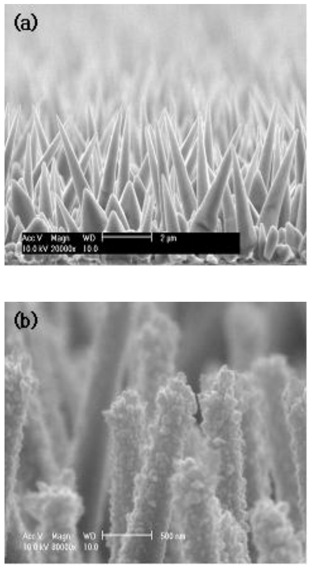

Figure 1 SEM images of (a) copper micro-tips, (b) Ni catalysts deposited on copper micro-tips

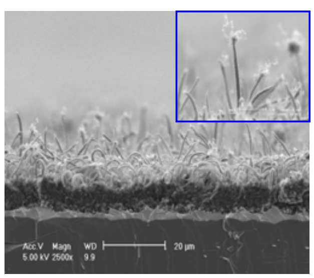

Figure 2 SEM images of CNFs.

In fact, we are investigating this phenomenon. It is believed that feeding gases are more activated by strong electric field around the copper micro-tips [12] and increasing impingement rate of feeding gases on local catalyst due to dense copper micro-tips which have much shorter inter-space than mean free path of feeding gas.

Figure 3 shows Raman spectra of the CNFs grown on copper micro-tips. The wavelength of the excitation laser was 514.53 nm. The peak of tangential C-C stretching (G) modes appears at approximately 1580 cm^{-1}, suggesting that the carbon nanostructures are multiwalled tubes or carbon nanofibers with crystalline graphitic sheets. The peak which originates from finite size effects or lattice distortions located at approximately 1335 cm^{-1}(D mode) is also observed, indicating the existence of amorphous carbonaceous particles or defective graphite layers in the wall.

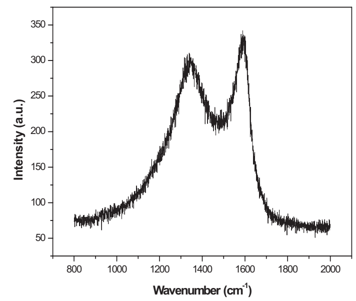

Figure 3. Raman spectra of CNFs.

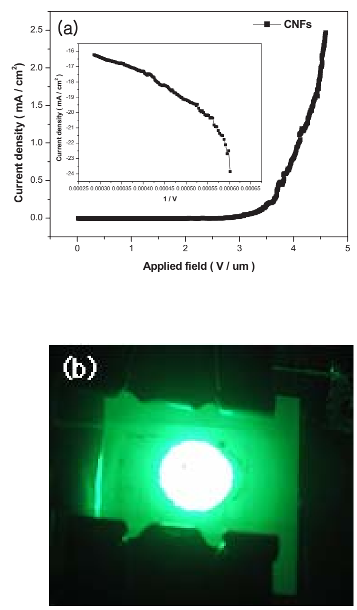

Figure 4. (a) I-V curve & F-N plot, (b) emission image of CNFs.

Figure 4 (a) shows current-voltage (I-V) curves with Fowler-Nordheim plots for the CNFs. The measurements were carried out several cycles and the results show consistent characteristics. It was observed that the CNFs showed a turn-on field of 2.9 V/μm with the current density of 10 μA/cm^2 and produced the current density of 2.46 mA/cm^2 at 4.59 V/μm. Figure 4 (b) shows emission image of the CNFs in the vacuum chamber. We observed uniform emission sites, as well as stable emission current, with the present CNFs.

Conclusion

We synthesized CNFs at low temperature using electroplated Ni catalyst formed on copper micro-tips to enhance the field emission characteristics. The CNF has a long length solid structure without hollow cores and branch of protrusions at the tip. It is believed that reactant gases are more activated by strong electric field around the tip and increment of their impingement rate in local area due to the copper micro-tips. The turn-on voltage of the CNFs was about 2.9 V/㎛ with an emission current density of 10 ㎂/cm^2, and the maximum emission current density of 2.46 mA/cm^2 was observed over the area of 0.2827cm^2, at the electric field of 4.59 V/㎛. We think that the good field emission characteristics of CNFs are due to long length of CNFs, and the small tip radius of protrusions.

Acknowledgement

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