

Study on Field Emission Properties of Carbon Nanotubes Grown on Different Metal Substrates

Dongyao Wei, Weilong Li*, Mi Hea and Zhaoyu Ren

National Photoelectric Technology, Functional Materials and Application of Science and Technology International Cooperation Center, and Institute of Photonics and Photon-Technology, Northwest University, Xi'an 710069, China

*Corresponding author. Email: lwl@nwu.edu.cn

Abstract. In this study, we fabricate the carbon nanotubes (CNTs) on different metal substrates via a simple and economic growing process by using a spraying device to inject the catalyst into the reaction chamber. The microstructure and field emission properties of the CNTs grown by three different metal substrates are researched. The results show that the CNTs grown on the high-voltage aluminum alloy substrate have optimal field emission properties. The turn-on electric field and threshold electric field is 0.92 V/ μm and 2.58 V/ μm respectively and the field enhancement factor is 20930. Lastly, the field emission current stability of the CNTs is tested, finding the field emission current of the CNTs grown on the high-voltage aluminum alloy substrate is the stablest. The high current density and good stability demonstrate that the CNTs grown on the high-voltage aluminum alloy substrate could be the promising and highly efficient field electron emitters.

Keywords: carbon nanotubes, field emission, metal substrates.

1. Introduction

The carbon nanotubes (CNTs) are regarded as the most promising field electron emitter thanks to its excellent electrical property, thermal conductivity, chemical inertness, tensile strength, small tip curvature and large length-diameter ratio, etc. The CNTs could remarkably enhance the local electric field of electron emission tip [1]. Therefore, the CNT film as cold cathode electron source is extensively applied to various vacuum electron devices, including microwave amplifier [2], vacuum microwave tube [3], flat-panel display [4], X-ray tube [5]. Due to its potential application to the semiconductor industry, CNT is usually grown on silicon wafer. Nevertheless, silicon is not the optimal substrate material in the application scenario requiring high conductivity and thermal conductivity. Furthermore, the contact resistance of multi-walled carbon nanotube (MWCNT) with the metallic substrate is smaller than that with the silicon substrate. So, it is all-important to grow CNTs on proper metallic substrate without impairing the performance needed by expected application. For example, Hordy et al. [6] directly prepares MWCNT on stainless steel substrate via the chemical vapor disposition (CVD) technology without any post-treatment, finding that the prepared CNTs are firmly bonded with the substrate. However, as chromium-rich passivation layer exists on it, it is difficult to efficiently grow CNTs on the appearance of original stainless steel substrate [7]. Thus, usually different strategies are used to activate the material in order to improve the quality and quantity of the

CNTs grown on stainless steel substrate, such as machine glazed finish, acid etching, plasma bombardment, oxidation and oxidation-reduction treatment [8].

Another alternative is just to increase the buffer layer on the metallic substrate to grow high-quality CNTs. Dubosc et al. uses nickel as catalyst and titanium as buffer layer to synthesize the CNTs on copper film via plasma enhanced chemical vapor deposition (PECVD) technology [9]. Copper, which has full-filled three-dimensional track, is difficult to form covalent bond with the hydrocarbon molecules. In the meanwhile, the small bond energy between copper and carbon inhibits the graphitization process. Besides, with low-carbon solubility, copper is hard to form carbon atom saturation needed by CNT structure [10]. To cope, a very thin buffer layer should be deposited on the copper substrate before depositing the nickel catalyst layer, to guarantee synthesis of the CNTs and satisfactory bonding with the substrate. In the existing research, the catalyst and buffer layer are mostly deposited on the metallic substrate via nanosphere technology, electron beam lithography, focused ion beam lithography, beam evaporation, pulsed laser deposition and magnetron sputtering [11], etc., which preparation methods, however, have complicated growing process and high cost. The defects of technological and economical limit them to be only applicable in lab. Therefore, to prepare CNTs on metallic substrate on a large scale needs a simple, extensible and economical preparation process.

This study grows CNTs on different metal substrates by a simple method of spraying chemical vapor disposition without the need for depositing the catalyst and buffer layer in advance. The CNTs are successfully prepared on three metallic substrates of copper foil, stainless steel, high-voltage aluminum alloy by controlling the growth temperature, growth time, gasses proportion, catalyst concentration and gases flow. The microstructure of the CNTs is characterized using scanning electron microscope, transmission electron microscope and Raman spectra. A comparative study is conducted on the field emission properties of the CNTs grown on three metal substrates using flat anode measuring system under high vacuum condition. The results indicate that the CNTs grown on the high-voltage aluminum alloy substrate have optimal field emission properties.

2. Experimental

The CNTs could grow on different metal substrates depending on CVD technology. First of all, the growth process of the CNTs on the copper foil substrate was as follows: a copper foil substrate was placed in the middle of a quartz boat, and the quartz boat was slowly pushed into a flat temperature zone of the quartz tube. Then, a certain amount of carrier gas (Ar) was fed to discharge air from the tubes. Under argon protection, the temperature rose to 750 °C at a rate of 25 °C/min. Then, hydrogen was fed to create a CNT growth environment (Ar : H₂ = 8:2). Acetylene was used as a carbon source, and no catalyst was fed. Acetylene flowed into the quartz tube at a flow rate of 30 sccm, and underwent pyrolysis under high temperature. Besides, a layer of carbon deposit was formed on the copper foil surface. Solution mixed with ferrocene and xylene (0.1 g/ml) was selected as a catalyst, and was injected into the quartz tube through a syringe (flow rate controlled). A spray device was used to reduce the diameter of the gas inlet to a small size (about 0.4 mm). This allowed gas to quickly flow at the inlet, a liquid catalyst inlet with a same diameter was connected to a gas inlet so that the liquid catalyst entered a reaction zone of the CVD furnace along with quickly sprayed gas. After the catalyst was fed, the flow rate of acetylene was adjusted to 20 sccm, and the growth time of the CNTs was 8 min. Afterwards, the CVD system was cooled to room temperature under argon protection. The process of CNT growth on a stainless steel substrate was substantially the same as that on the copper foil substrate, and the growth time was changed to 12 min. The CNTs grew on a high-voltage aluminum alloy substrate without carbon deposit, and catalyst was fed together with acetylene (growth temperature: 700 °C; acetylene flow rate:10 sccm; catalyst concentration: 0.06 g/ml; growth time: 6 min). The CNTs were successfully prepared on three different metal substrates.

3. Results and discussion

The growth mechanism of the CNTs is as follows: the growth temperature is selected because the catalyst particles are under enough temperature to achieve a desired semi-liquid state, thus maintaining the growth of the CNTs. A carbon matrix precursor on the outer surface of the catalyst particles was decomposed depending on energy generated during heating, so that carbon from acetylene pyrolysis reacts with the iron catalyst to form clusters or intermediate carbides. The carbon atoms diffuse in the catalyst particles, while a tubular structure is formed on the catalyst particles. This is a process in which carbon species are constantly absorbed on the catalyst surface, resulting in excess carbon. Excess carbon will grow into the CNTs at a rate proportional to the carbon atom feed rate of the iron catalyst nanoparticles. Fig.1 shows the images (at different magnification) of the CNTs growing on different metal substrates from the scanning electron microscope. Fig.1 (a) shows that the CNTs sparsely grow and are evenly distributed on the copper foil substrate. Fig.1 (b) shows that the CNTs have a large diameter, and their tips are upward. Fig.1 (c) shows that the CNTs grow in disorder and are unevenly distributed on the stainless steel substrate. Fig.1 (d) shows that the CNTs are smaller than those growing on the copper foil substrate in diameter. Fig.1 (e) shows that the CNTs densely grow and are evenly distributed on the high-voltage aluminum alloy substrate. Fig.1 (f) shows that the CNTs are significantly smaller than the first two in diameter, and the tips of the CNTs are clustered together. The CNTs growing on different substrates presented different field emission properties due to the differences in the distribution density and diameter of the CNTs.

In order to further study the morphological characteristics of the CNTs, transmission electron microscope analysis is conducted. Fig.2 shows the local structure of the CNTs on different substrates at ultra-high magnification. The synthetic products are of hollow tubular structure, mostly multi-walled structure. The diameter of the CNTs growing on different metal substrates can be obtained. Fig.2 (a) shows that the inner and outer diameters of the CNTs growing on the copper foil substrate are about 28 nm and about 38 nm respectively. Fig.2 (b) shows that the inner and outer diameters of the CNTs growing on the stainless steel substrate are about 15 nm and about 20 nm respectively. Fig.2 (c) shows that the inner and outer diameters of the CNTs growing on the high-voltage aluminum alloy substrate are about 8 nm and about 11 nm respectively.

Raman spectroscopy is a contactless and non-destructive tool for characterizing the microstructure of the carbonaceous materials, and is also one of the most common technologies for identifying the graphitization or structure of the CNTs. Fig.3 shows the typical Raman spectrums of the CNTs growing on different substrates, ranging between 900 and 1800 cm^{-1} . It can be seen that the spectrum has similar characteristics, ranging between around 1340 and 1590 cm^{-1} (namely D peak and G peak), as the typical characteristics of the multi-walled CNTs. The intensity ratio of Peaks G and D is generally used to evaluate the structural integrity of the CNTs, and high I_D/I_G shows that the multi-walled CNTs exhibit a very high defect density.

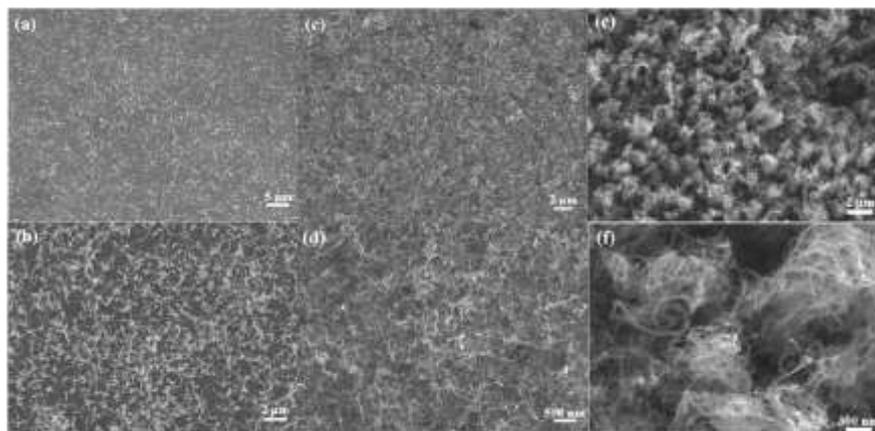


Figure 1. (a-b) SEM images of the CNTs at different magnification grown on the copper foil substrate; (c-d) SEM images of the CNTs at different magnification grown on the stainless steel substrate; (e-f) SEM images of the CNTs at different magnification grown on the high-voltage aluminum alloy substrate.

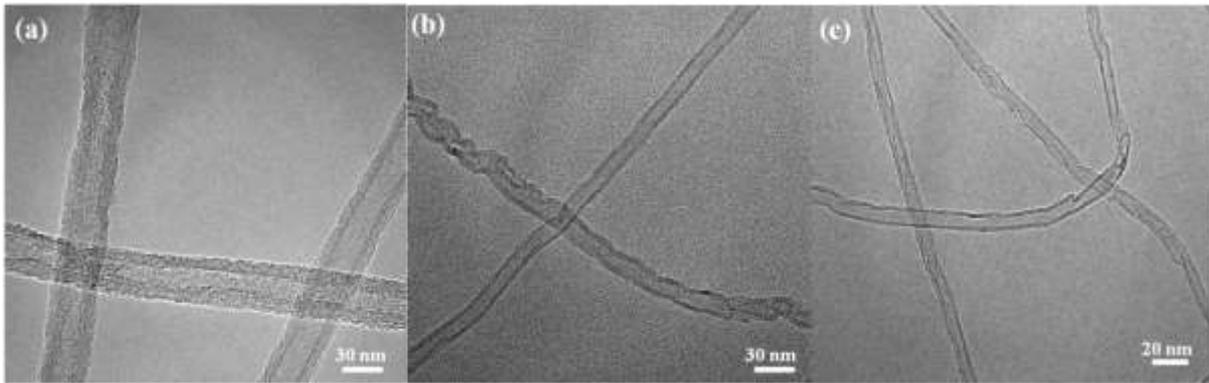


Figure 2. (a) TEM images of the CNTs grown on the copper foil substrate; (b) TEM images of the CNTs grown on the stainless steel substrate; (c) TEM images of the CNTs grown on the high-voltage aluminum alloy substrate.

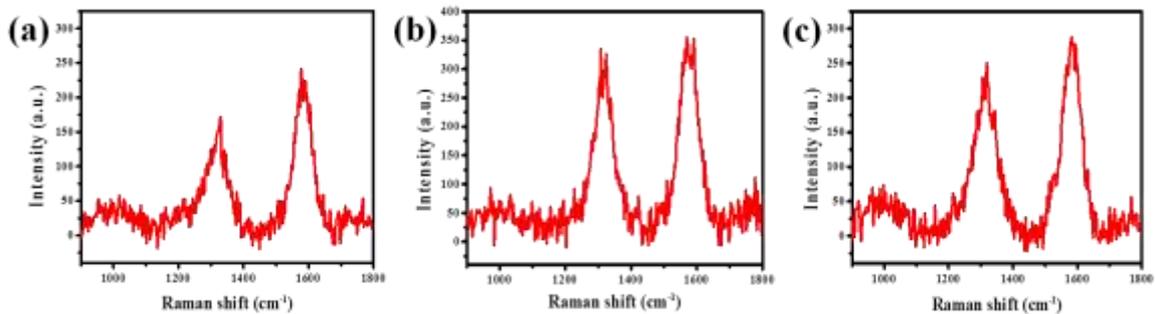


Figure 3. (a) Raman images of the CNTs grown on the copper foil substrate; (b) Raman images of the CNTs grown on the stainless steel substrate; (c) Raman images of the CNTs grown on the high-voltage aluminum alloy substrate.

The field emission properties of the CNTs growing on the three metal substrates are tested by a field emission test instrument, and each measurement is repeated 5 times, so as to determine the repeatability of the field emission properties. Fig.4 (a), (c) and (e) show the changes in the field emission current density of the CNTs growing on three different CNTs with applied electric field ($J-E$). Fig.4 (b), (d) and (f) also give corresponding $F-N$ charts. Fig.4 (a) shows that the CNTs growing on the copper foil substrate has poorer field emission repeatability, because the $J-E$ curve from the first three tests presents great deviations. Fig.4 (c) shows that the CNTs growing on the stainless steel substrate has good field emission repeatability. Compared to the first two, multiple measurements demonstrate that CNTs growing on high-voltage aluminum alloy substrate have good field emission repeatability (Fig.4 e). This is because the CNTs growing on the high-voltage aluminum alloy substrate is significantly better than those on the copper foil and stainless steel substrates in respect of even distribution. In addition, the results of 5 consecutive field emission tests in Fig.4 (e) shows that the first field emission test has the lowest turn-on field and threshold field, considering that a few carbon deposition occurs at the tips of the new CNTs, and carbon deposition at the tips of the CNTs can be deemed as a field emitter. The carbon deposition field emitter will increase the field emission current, thereby reducing the turn-on electric field and threshold electric field. However, due to

unreliable adhesion between the deposited carbon and the CNTs, deposited carbon will fall off under strong electric field. Therefore, the second field emission test shows that the current density slightly decreases under the same applied electric field, and subsequent tests show stable field emission properties. Table 1 intuitively gives field emission data of the CNTs growing on different metal substrates. The turn-on field and threshold field of the CNTs growing on the high-voltage aluminum alloy substrate have the minimum intensity (0.92 V/ μm and 2.58 V/ μm respectively). This is because the CNTs growing on different metal substrates have different density, and the CNTs growing on the high-voltage aluminum alloy substrate are provided with more field emitters per unit area. Beside, higher current density can be obtained under the same applied voltage, thus resulting in smaller turn-on field and threshold field. The field enhancement factors of the CNTs on different substrates are calculated, and the maximum field enhancement factor on the high-voltage aluminum alloy substrate is 20930. The increase in the field enhancement factors can be attributed to a smaller diameter, and results in a higher local electric field under the same applied voltage. In addition, the tips of the CNTs growing on the high-voltage aluminum alloy substrate are clustered together, which reduces the field shielding effect and helps to increase the field enhancement factors.

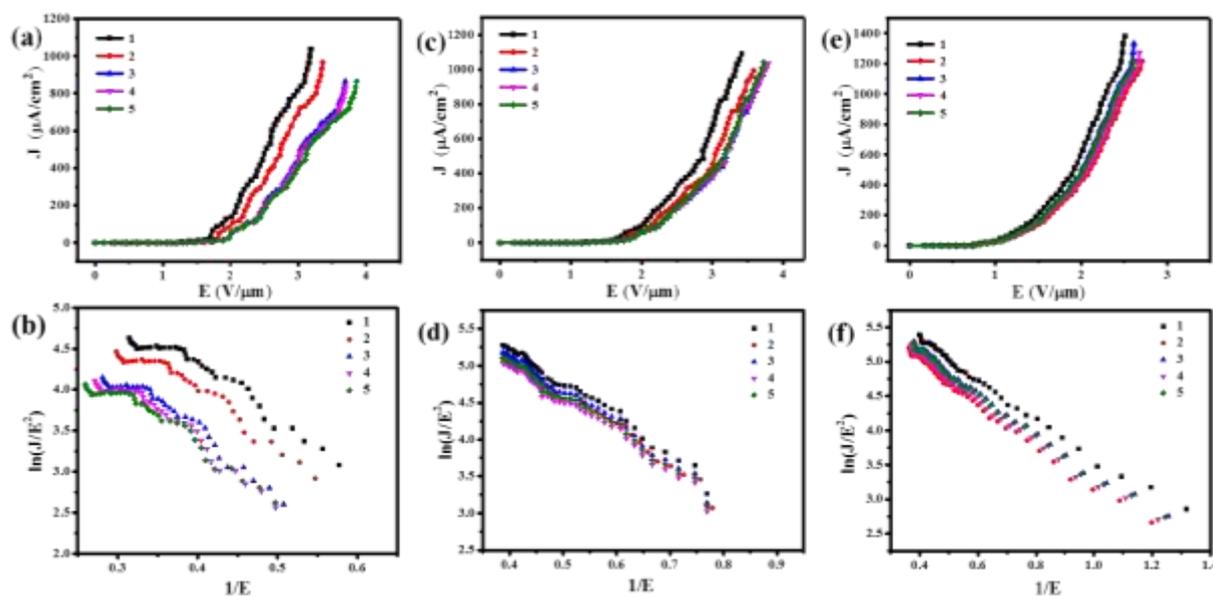


Figure 4. (a) Field emission Characteristics in J - E plots of the CNTs grown on the copper foil substrate; (b) Fowlere-Nordheim plots of the CNTs grown on the copper foil substrate; (c) Field emission Characteristics in J - E plots of the CNTs grown on the stainless steel substrate; (d) Fowlere-Nordheim plots of the CNTs grown on the stainless steel substrate; (e) Field emission Characteristics in J - E plots of the CNTs grown on the high-voltage aluminum alloy substrate; (f) Fowlere-Nordheim plots of the CNTs grown on the high-voltage aluminum alloy substrate.

Table 1. Field emission parameters of the CNTs.

	The turn-on electric field (V/ μm)	The threshold electric filed (V/ μm)	The enhancement factor
the CNTs on the copper foil substrate	1.89	/	6909
the CNTs on the stainless steel substrate	1.65	3.68	10797
the CNTs on the high-voltage aluminum alloy substrate	0.92	2.58	20930

The stability of the field emission current is one of the important parameters for evaluating the feasibility of various uses of the CNTs. Fig.5 shows the long-term discharge results of the CNTs growing on different substrates under an applied electric field of 2.6 V/ μm . Under the applied electric field of 2.6 V/ μm , the comparison finds that the field emission current of the CNTs growing on the high-voltage aluminum alloy substrate is the most stable, and the current density fluctuates within the range of 0.98-1.06 mA/cm². The current of the CNTs significantly fluctuates in the first minute due to uneven electric field at the tips of the CNTs. Therefore, the local electric field of the protruded CNTs is particularly high, and a part of the emitter of the protruded CNTs is burnt out. After the first minute, the field emission current density keeps stable at 0.98 mA/cm². After a 90 min field emission test, the field emission current density of the CNTs decreases slightly under the influence of degradation of the carbon nanotube emitter. This is possibly caused on gas absorption on the tip surface and thermal damage occurring during field emission. In Fig.5, the comparison finds that the CNTs growing on the high-voltage aluminum alloy substrate presented the minimum drop in respect of the field emission current density after long-time discharge, with stable field emission current, so the CNTs growing on the high-pressure aluminum alloy can become a good field emitter.

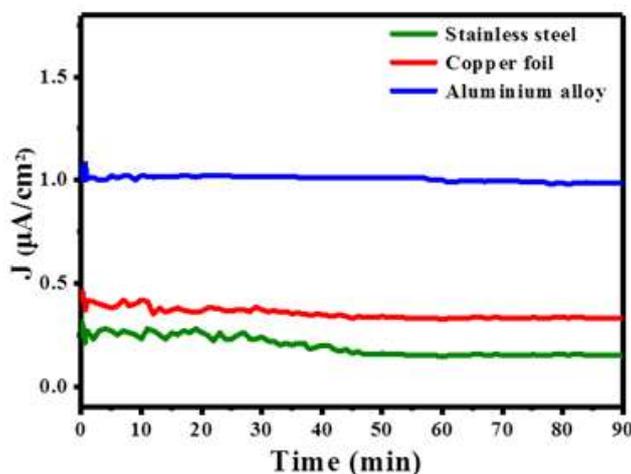


Figure 5. The results of long-term discharge of the CNTs under an applied electric field of 2.6 V/ μm .

4. Conclusion

In this work, we grew the CNTs via the CVD technology, which used the spraying device to inject the catalyst and gasses into the reaction chamber. The experimental conditions were controlled to prepare CNTs on three metallic substrates of copper foil, stainless steel and high-voltage aluminum alloy successfully. The test result of field emission showed that the CNTs prepared on substrate of high-voltage aluminum alloy had the optimal field emission properties, with turn-on field and threshold field being 0.92v/ μm and 2.58v/ μm , and field enhancement factor being 20930. Lastly, the current stability of field emission of CNTs was tested, with result proving the CNTs grown on metallic substrate had a stable long-term current emission ability. The high current density and good stability demonstrate that densified the CNTs grown on the high-voltage aluminum alloy substrate are the promising and highly efficient field electron emitters.

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