Chapter 3

Density Control of Carbon Nanotubes by Partial Oxidation of Catalyst Metals and its Field Emission Enhancement

The density distribution of carbon nanotubes is one of the critical parameters dominating the field emission characteristics of CNTs. Partial oxidation of metal catalyst is used to change the distribution of CNTs. The results show that this method can change the morphology of carbon nanotubes' growth and its field emission also can be enhanced. The turn-on filed is reduced to 1.9V/μm, the threshold field is reduced to about 3.9 V/μm and high field emission current density (160mA/cm^2) at an applied electric field of 6V/μm are achieved owing to effectively controlling of the density of CNTs.

3.1 Introduction

Electron field emission from nano-materials such as carbon nanotubes (CNTs) has been a wide and interesting field owing to their excellent electronic and structural properties. Several groups [3.1-3.8] have demonstrated the low turn-on electric field characteristics and high emission current density of CNT field emission diodes. In most works, arc-produced CNTs [3.7] and screen-printing techniques were used to fabricate low-cost CNT field emission diodes for field emission displays. However, specific purification processes for arc-produced CNTs are required, and the uniformity of screen-printed CNT field emitter arrays is so poor that it results in a non-uniform emission current. Selective growth of CNTs by chemical vapor deposition (CVD) processes is sufficient for fabricating field emission devices with excellent uniformity. However, the density of the CNTs, which is an important parameter dominating the field emission characteristics, cannot be controlled well by chemical vapor deposition processes such as thermal chemical vapor deposition and microwave plasma enhanced chemical vapor deposition (MPCVD)[3.8-3.10]. The effect of screening electric field by the dense arrangement of CNTs has been reported by several groups [3.11-3.13]. The electric field is screened out for the closely spaced CNTs, which results in a reduced effective electric field near the CNT emitters. As a result, the turn-on electric field is increased and the emission current density is decreased.

To obtain better field emission characteristics, the density of CNTs should be optimized. There are several methods to control the density of CNTs like different aspect ratios of anodic aluminium oxide (AAO) nanochannels [3.14], NH_3 plasma treatment of catalyst film [3.15], high density O_2 plasma post-treatment [3.16], excimer laser irradiation on CNTs film [3.17] and excimer laser nanostructuring of catalyst film [3.18]. In this study, partial oxidation of metal catalyst is used to change the distribution of CNTs. The experimental results reveal that high emission current density and low turn-on field of CNTs can be achieved.

3.2 Experimental Procedures

In this study, the fabrication procedures of CNTs are listed as below. A 1 μm-thick photoresist was spin-coated on an n-type Si (100) substrate and square cells with an emission area 25×10^{-4} cm^2 are patterned by photolithography. Then a Ti layer of 50nm and a thin Fe (~15 nm) catalytic layer are subsequently deposited on the photoresist patterned Si substrate by electron beam evaporation system. Afterward, the patterned film is formed after the photoresist is removed by the lift-off method. Finally, the patterned catalyst film is partial oxidation at 500°C for 2min and CNTs are grown in the atmospheric pressure thermal chemical vapor deposition.

The thermal CVD reactor is a 2-in.-diameter horizontal quartz tube furnace. Samples are placed horizontal up into the reactor at about 400˚C, and then be heated to 700˚C at 100˚C/min in pure N_2 with the flow rate at 1000 sccm. Then, the partial oxidation catalytic film is pre-treated in pure H_2 with the gas flow rate at 300sccm. The pre-treatment times are 10 min. Finally, CNTs are grown in C_2H_4 (20sccm)/ N_2 (500) mixture gases for 10min. Scanning electron microscopy (SEM) is used to examine the morphology of carbon nanotubes. The field emission tests are measured in a parallel plate diode configuration at room temperature in vacuum of ~ 5 x 10^{-6} Torr. The spacer between the anode and CNTs cathode is approximately 120 μm and the emitting area is 25×10^{-4} cm^2. The field emission current is measured as a function of the anode voltage.

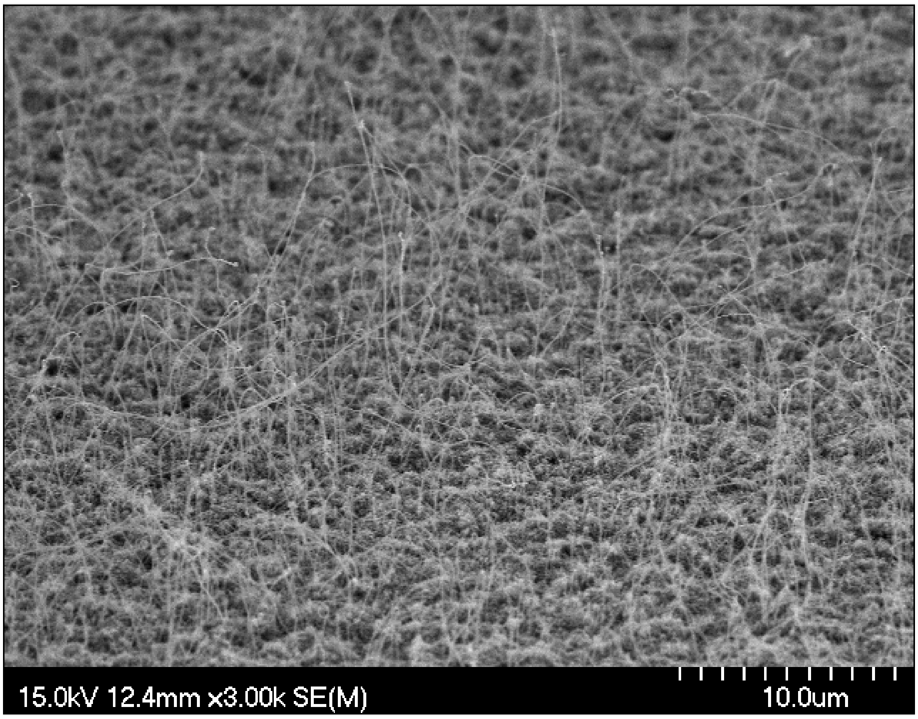
3.3 Results and Discussions

Figure 3-1 shows SEM images of CNTs grown using partial oxidation of metal catalyst. Figure 3-1(a) shows low magnification of top view. It is observed that the CNTs are aligned and closely spaced, and spilt into two groups with a few longer nanotubes protruding among them. Figures3-1(b)-3-1(c) show low and high magnification of 60°top views. The shorter CNTs are probably grown upward from the bottom and end with an oxidation layer of catalyst. A lot of thinner CNTs are also observed above the oxidation layer of catalyst. Those protruding CNTs are aligned and grown from the bottom. They are probably grown from nanoparticles of catalyst which is reduced during H_2 pretreatment process. The flat top of the shorter group of CNTs tends to result in the screening effect of the electric field during cold cathode operation. The field enhancement factor therefore decreases and the CNT emitter has poor field-emission properties. Alternatively, the screening effect can be reduced in the longer group of CNTs that has a relatively low density of CNTs than the flat top of shorter set of CNTs. Finally, the longer set of CNTs will emit electrons at lower electric field than the flat top of CNTs due to a relatively low density. Figure3-1(d) shows the cross sectional view of of CNTs grown using partial oxidation of metal catalyst. Those protruding CNTs are about 10 μm or more and the short group of CNTs is about 4 μm.

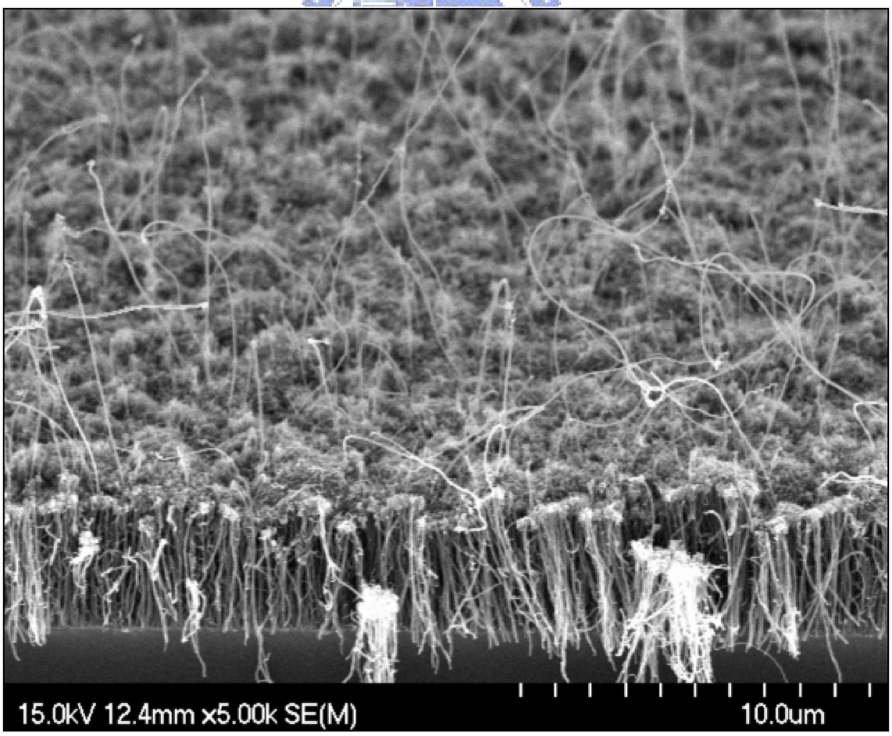
Figure 3-2(a) shows the field-emission characteristics of CNTs grown using partial oxidation of metal catalyst. The corresponding Fowler-Nordheim plots are shown in Fig. 3-2(b) and the linearity of the F-N plot confirmed the field-emission phenomenon. The turn-on filed is reduced to 1.9V/μm, the threshold field is reduced to about 3.9 V/μm and high field emission current density (160mA/cm^2) at an applied electric field of 6V/µm can be achieved owing to effectively controlling of the density of CNTs.

3.4 Conclusions

In this study, we proposed an effective way to control the density of CNTs using oxidation of metal catalyst before CNTs' growth. By changing the oxidation temperature or oxidation time, it is possible to control the density of CNTs in the longer group. The results showed that this method could change the morphology of carbon nanotubes' growth and its field emission could also be enhanced. The turn-on filed is reduced to 1.9V/μm, the threshold field is reduced to about 3.9 V/μm and high field emission current density (160mA/cm^2) at an applied electric field of 6V/μm can be achieved owing to effectively controlling of the density of CNTs.

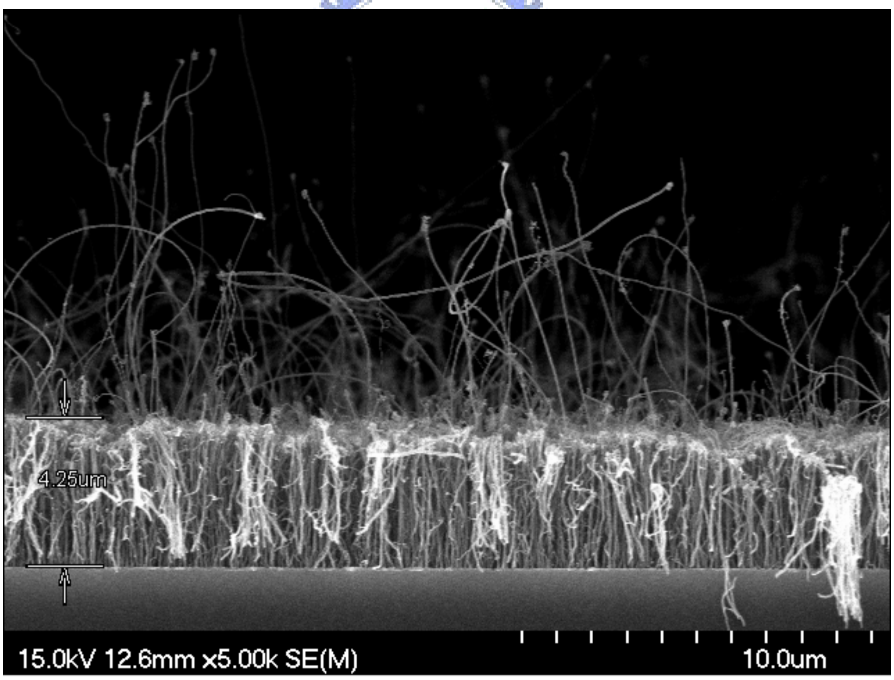


(a)



(b)

(c)

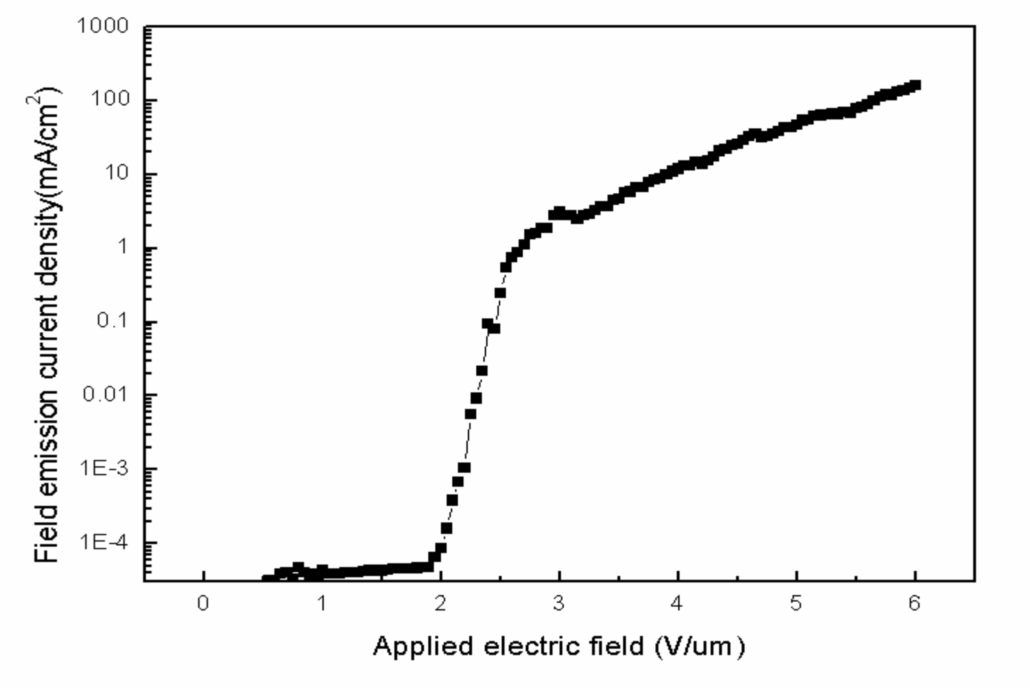


(d)

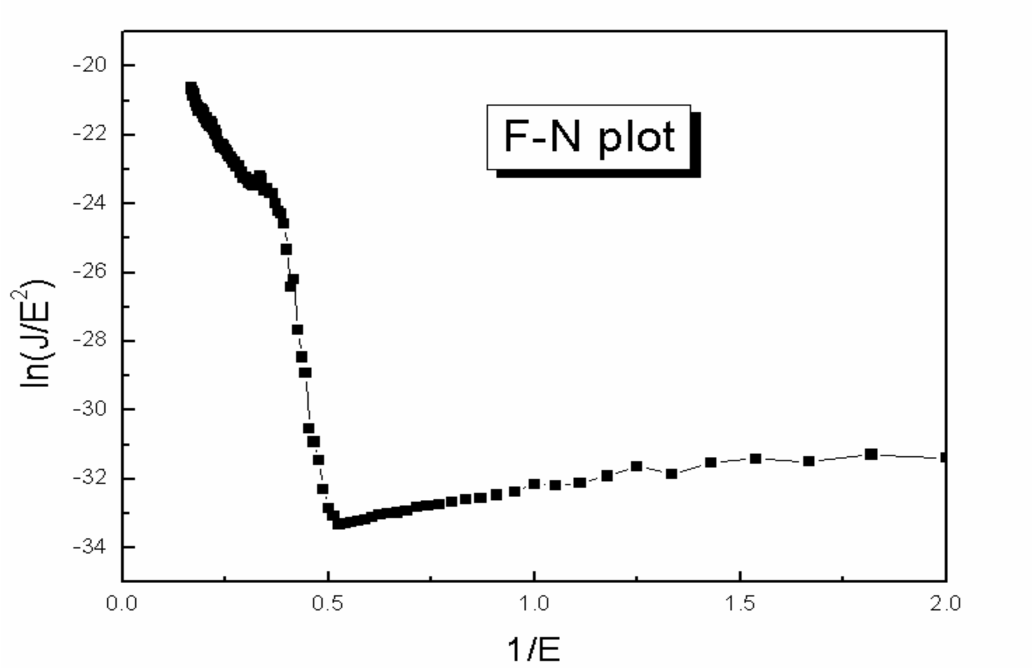
Figure 3-1 SEM images of CNTs grown using partial oxidation of metal catalyst

(a) low magnification of top view (b) low magnification of 60° top view

(c) high magnification of 60° top view (d) the cross-sectional view.



(a)



(b)

Figure 3-2 Field emission characteristics of CNTs grown using partial oxidation of metal catalyst (a) Field-emission current density vs applied electric field. (b) Corresponding F-N plot