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# Design and Demonstration of Carbon Nanotubes (CNTs)-Based Field Emission Device

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## 1. Introduction

Since its discovery, carbon nanotube (CNT), possessing a series of particularly electrical and mechanical property as well chemical stability, has been considered as one of the most advanced electronics materials. A lot of research has been extensively carrying through on CNTs' potential applications for instance, gas storage, quanta lead, electron device, catalyst carrier, and etc. Among its various applications, more talked is its application as field emission cathode (FEC) material to make large-area, full-colored and high efficiency displays or lighting devices (FEC-LED) because of its excellent field emission property. Compared with the other material of field emission cathode, CNT-FEC devices have a series of unique performances, such as higher field emission efficiency, lower power consume, lower cost, non pollute problem in its production processes, and so on. Those advantages come from the following physical and chemical mechanism:

1. CNT possesses so large aspect ratio in structure that the field enhancement factor CNT can reach 30000 to 50000 for single CNT, 800 to 3000 for CNT film, no matter what state, standing or lying they are. Therefore CNT is such an excellent field emitter that CNT-FEC can easily provide necessary current under a lower drive voltage with much lower power consume.
2. CNT-FED workmanship is simply, the material cost is low. When the manufacture is enlarged, it can compete with other technologies of display or lighting devices in price.

On the other hand there are still some theoretical and technical problems need to be solved before CNT-FED being get more competitive applications on the market, for example, its feasibility of a large scale production, full colored field, optimal structure design, spatial homogeneity, stability, lifespan, as well as its low cost fabrication technology. this chapter mainly concerns these problems mentioned and gives some elementary discussion in for our further understand of them, including :

- The research on the field emission properties of CNT and computer simulation based on Fowler-Nordheims theory;

- The research on influence of relative height between cathode and gate on electron transmission efficiency.
- Structural Analysis on a Field Emission Display Panel Based on CNTs.

## 2. Research on the field emission properties of CNTs

### 2.1 The main points and technical background

The theory on CNT's field emission is a base for FED theoretical analysis and optimal design, which deals closely with device efficiency, power consume, operation stability, life time, and so on. There are a lot of different viewpoints on the mechanism of the CNTs field emitters. Some researchers approved an idea that the CNTs field emission accords with the Fowler-Nordheims tunneling theory and the electrons are emitted from the top of CNTs, whose work function approaches the value of graphites. On the other hand, Collins, Zettle and Bonard<sup>[2]</sup> considered that: the CNTs field emission is more complex than the one expected by F-N tunneling theory. They proposed a new CNT field emission prototype. Gulyaev<sup>[3]</sup> believed that: the closely relationship of field emission with temperature for both single-walled and multi-walled CNTs shows that the CNTs are low work function field emitters. But Rinzler<sup>[4]</sup> held that the CNTs are very sharply high work function emitter. The reason why the CNTs field emission increasing with a high temperature is due to the carbon atom's reconstruction on the tip of CNTs, resulting in the increasing field enhancement factor. Dean *et al*<sup>[5]</sup>, divided the field emission of carbon into three processes: adsorption state, clean state and high current state. We have also observed in our experiment that the properties curve of CNT field emission is not a strict straight line, which changes with the electric field intensity. So we established a simple prototype to explain the observed CNT emission characteristics. The main research result is that the F-N curve's non-linear in experiment can be explained as the disappearance of adsorbate (mainly H<sub>2</sub>O) , which changes the effect work function of CNTs. When they are bombarded by the remained gas particles in device, the tube caps are flattened and their lengths shortened, resulting in its electron emission contribution of short CNTs to total currents enhancing with the increase of electric field intensity.

### 2.2 Experiment description

The adopted CNTs are produced by chemical vapor deposition (CVD), and observed by electron microscopy. The CNT material purity is very high and having a lot of CNTs to aggregate and tangle together generally, so they need to be dispersed with ultrasonic process. We take a proper amount of CNTs powder and pour it into acetone liquor and then ultrasonic process for more than half an hour. Sucking the suspension of CNTs through filter paper and air dried thoroughly, then mix the dry CNTs with silver paste. Because of the highly viscosity of silver paste, it must be mixed adequately with special tool, and then repeated it like this several times until the content of CNTs is appropriate. Thus enough emission current can be not only got, but also the field shielding effect between adjacent CNTs can be avoided. The mixture of silver paste and CNTs is printed on the clean glass substrate by silk-screen printing technology, put in muffle furnace, and then heated at 300°C for half an hour, making silver paste solidified. On one hand the silver paste can solidify the CNTs, on the other hand; it makes the CNTs emission electrons supply continually. Resulting from the different melting point between CNTs and silver paste, a trench is etched on the silver paste. By adjusting the energy and scanning speed of laser beam, not only the silver paste should be etched, forming electrical

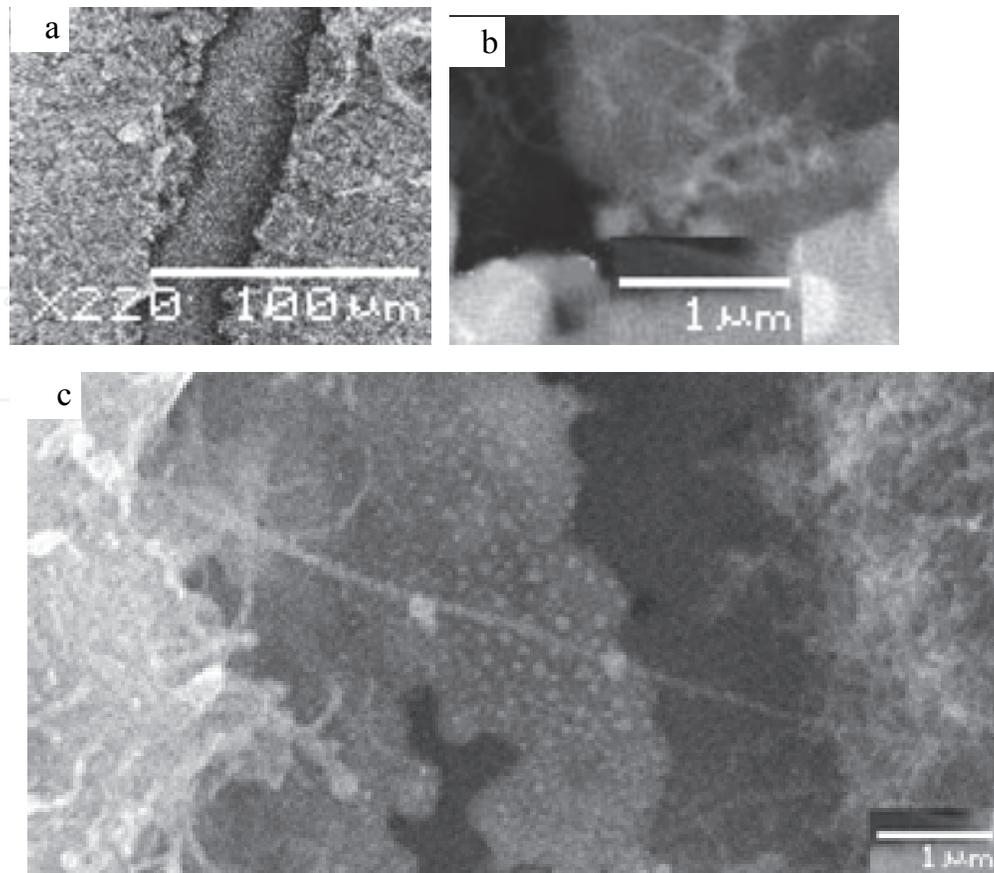


Fig. 1. (a) a trench etched with laser; (b) carbon nanotube on the edge of trench; (c) a carbon nanotube with the length of 5μm

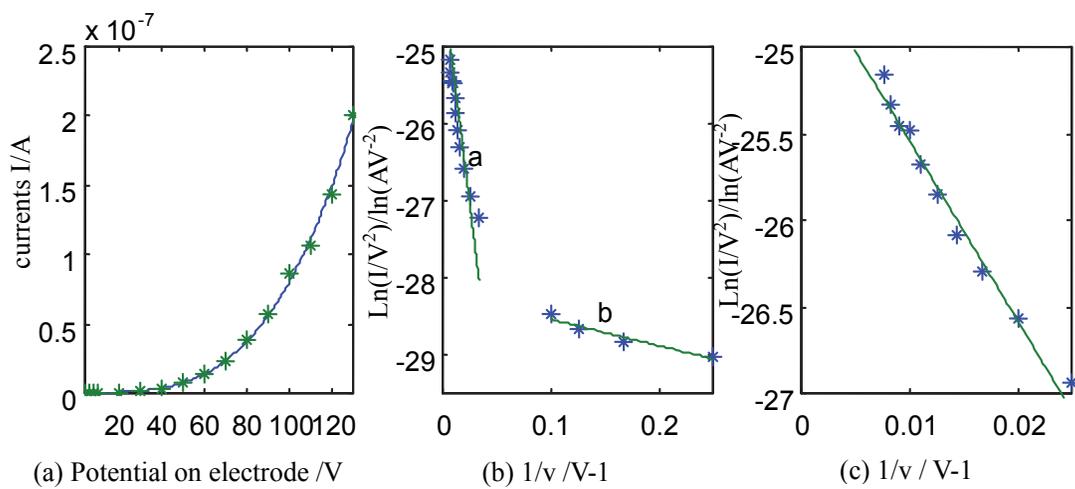


Fig. 2. (a). Emitting current vs. Voltage, (b). F-N plot (Potential ranged from 4V~130V) (c). F-N plot (Potential ranged from 40V~130V)

insulation between the cathode and gate (the resistance between the cathode and gate should be more than 50MΩ at least), but also ensuring CNTs left at the edge of the trench. Then the field emission character of CNTs on both side of trench can be measured in vacuums with a low current testing instrument (such as Cathely 6517A). Fig.1(a) shows

that a trench is etched on the silver layer mixed with CNTs by laser beam, in the middle of which there are some little silver particles left, whose width is about 35 $\mu\text{m}$ . There are some CNTs on both side of the trench, rarely seen them in the middle of trench, which is likely to be sputtered out with the silver particles. In the trench some longer CNTs can be observed occasionally. Seeing Fig. 1(c), the length of a CNTs outside of the silver layer in trench is about 5 $\mu\text{m}$ . The edge of the trench is not very even and the length of CNTs is not the same.

The character of CNTs field emission is shown as Fig. 2, which shows that the curve of CNTs field emission matches very well with F-N curve when applied voltage between the electrodes exceeds 40V ; while flatten a lot, when less than 40V. (shown as curve b in Fig. 2 (b)).

### 2.3 Theoretical prototype and analysis

In field emission experiments, the measured F-N curve is not a strict straight line which has a little difference compared with the result deduced from the F-N Theory. As curve b in Fig. 2(b), this is a relatively common phenomenon, but people trend to show the emission characteristic curve in specific voltage range, such as a curve in Fig. 2c. We have seldom seen somebody explain the phenomenon shown as in curve a) and b) in Fig. 2b. From the F-N formula,

$$\frac{i(L)}{A} = (1.54 \times 10^{-6}) \frac{\beta^2(L)V^2}{\phi} \exp\left(-\frac{6.83 \times 10^7 \phi^{3/2}}{\beta(L)V}\right) \quad (1)$$

In equation (1),  $L$  is the length of CNTs and  $A$  is the effective emitting area of CNTs. It can be observed that only two parameters that influence the F-N curve slope, namely, the field enhancement factor  $\beta$  and work function  $\phi$ . For CNTs,  $\beta$  has something with the length, radii, and the shape of the CNTs, while  $\phi$  relates with the CNTs adsorption. In order to explain the reason why the F-N curve slope in experiment changed with the voltage changing, let us to suppose that the length distribution of CNTs at the edge of the trench obeying with normal distribution, and CNTs shape at the up end and their radii are the same, and each CNT field emission is independent of different field enhancement factor  $\beta(L)$ . So the total field emission current  $I$  is:

$$I = \sum_l G(L)i(L) \quad (2)$$

In equation (2),  $G(L)$  is the number of the CNTs with the length distributed in the range of  $L \pm 0.2\mu\text{m}$ , if some of the CNTs is shortened at the higher emission current because of heat or bombardment of the charged particles (in fact, the disappearance of some kind protruding parts on the top of CNTs can be considered in the same way as that of shortening the length of CNTs), so at different voltage, the length of CNTs have different cutoff values, which impact the CNTs field enhancement factor. Fig. 3 show the F-N curves at two different work function and five different cutoff lengths. It can be seen that the shorter cutoff length is, the greater the work function is, and the greater the slope of curves is. To be simple, we supposed that the expected value of the CNTs length is 3 $\mu\text{m}$ , whose mean square deviation is 1 $\mu\text{m}$ , and all the radii of CNTs is about 3nm. There are several methods about the calculation of the field enhancement factor, for different length ranges [6,7]. We make use of the calculation method  $\beta(L) = KL/r$  commonly used for CNTs. Here  $K$  is the statistic of the

previous field enhancement factor and a correctable coefficient given when we choose CNTs length ranges. Now the experimental phenomena can be explained below: At the low voltage, the emission current is mainly emitted from longer CNTs, but little from shorter ones. The longer the CNTs are, the greater the field enhancement factor is, and the smaller the slope of F-N curve is. During this stage, the field emission process is dominated by the CNTs in absorbate formed by water vapor, which can be formed into the C-H-O-H bond on the surface of CNTs, and reduces the effective work function of the CNTs surface<sup>[8]</sup>. These two factors result in a smaller F-N curve slope ( $\phi^{1.5}/\beta$ ) at the beginning of the CNTs field emission.

As the electric field intensity increases further, the CNTs field emission current increases and the tiny protuberances on the tip of CNTs are melted or smoothed under bombardment by residual gas particles. Meanwhile, the absorbate on the top of CNTs is also removed, and then the effective work function increase to 5 eV, which is equal to that of net carbon. It can be seen that the shorter CNTs and the greater work function will lead to the greater slope of F-N curve, and the contribution of shorter CNTs to field emission is growing with the increasing of electric strength on the top of CNT. Fig. 4 show the values of CNTs field emission current at different voltage and different cut-off lengths ranged from 1 $\mu\text{m}$  to 4.7 $\mu\text{m}$ , to a certain cut-off length, the lengths of CNTs follows the Gaussian distribution. It can be seen that: When the applied voltage is lower (such as 6V), the emission current is mainly contributed by CNTs of length 4.6 $\mu\text{m}$  or more; When the applied voltage increases to 130V, the current emitted by CNTs with length of 2.8 $\mu\text{m}$  or more will contribute a large proportion to the total. So we can get a conclusion: with the reduction of CNTs length and increasing of its work function according to improvement of the voltage, the slope of the F-N curve becomes more flat, When the applied voltage is more than 40V, the field emission is mainly adopted by clean CNTs with work function of about 5eV, and the F-N curve strictly follows a straight line ( shown as Fig. 2(c))

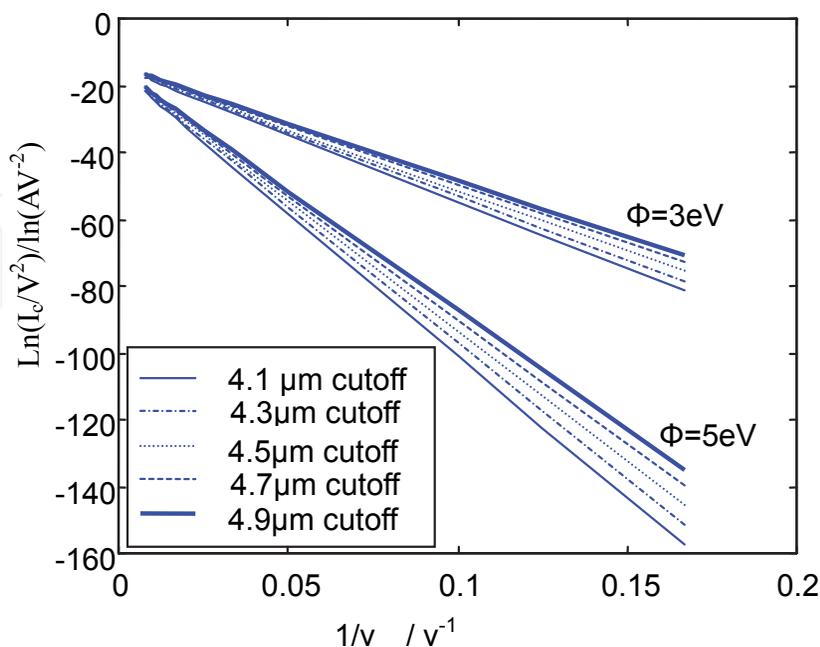


Fig. 3. F-N curves of different cutoff length and work function

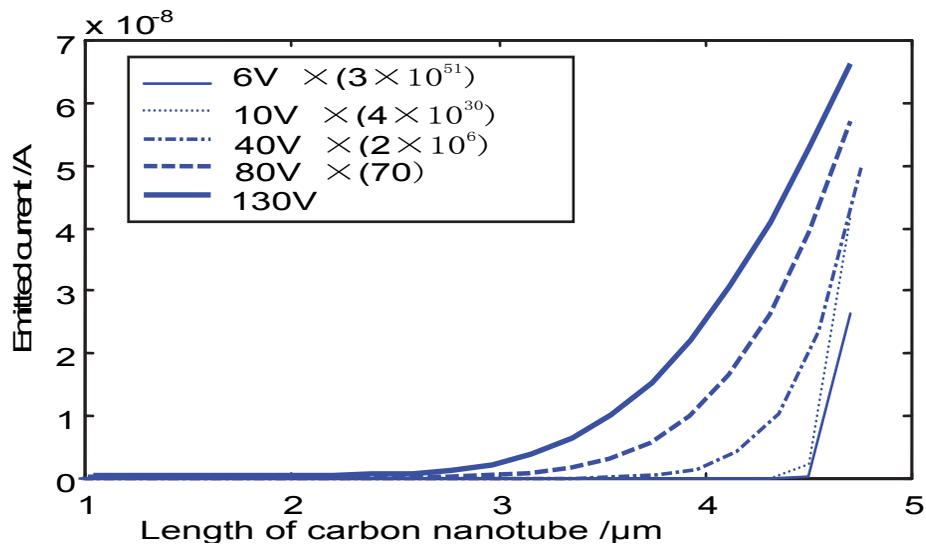


Fig. 4. illustrating the varying contribution of tube length to total current  $I$ , for different anode potentials  $V$ .

## 2.4 Conclusion

There are lots of field emission experiments about CNTs, but in many cases they just show some field emission characters in specific voltage ranges, thus the result of experiments matching well with F-N curves. Although some experiments get the CNTs field emission character both at low and high electric field intensity, there are no reasonable explanation about them. Based on the F-N tunneling theory, a simple prototype has been established in the paper, which explains well the phenomenon that the slope of F-N curve changes with applied electric field intensity in the process of CNTs field emission. The main reason for increasing of F-N curve slope is considered that the adsorbate plays a big role at the beginning of field emission, and then the field emission of carbon atoms on the surface of CNTs becomes dominated gradually. Meanwhile, as the voltage increasing, the protuberance on the top of CNTs disappears by bombardment of the remained gas particles. In fact, the CNTs field emission is much more complex. First of all, the CNTs itself can be classified into metallic and semiconductor according to the chirality. Secondly, the type of materials adsorbed on the surface and their locations on top of the CNTs are all changed, and the emission area is also a transformable factor. Consequently there will be lots of theoretical and experimental work needed to be carried out if we want to have a more intensive understanding about the process of CNTs field emission.

## 3. The Influence of relative height between cathode and gate on electron transmission efficiency

### 3.1 The key points and technical background

This topic associates with the structure optimization design for a kind field emission display (FED), among the parameters affecting FED performance, the relative height between cathode and gate plays an important role because it dominates FED electron transmission efficiency directly. The electron trajectories as well as their distribution on anode in a large area-full colored FED prototype have been theoretically analyzed by using Monte Carlo and Boundary Element Methods. The result has been used to improve the electron transmission

efficiency via adjusting the vertical distance between cathode and gate, at the same time, the elevation angle of CNT on the influence of transmission efficiency is also discussed.

It is noted that the surface conduction electron emitter displays<sup>[1]</sup>(SCED) proposed by Canon Corporation has simplified production process of FED, and provided a feasible way for FED with large area. According to the technical information, the electron transmission efficiency(the ratio of electron to the anode and electron to the cathode) of this kind is no more than 1%, so we proposed two solutions to try to improve it <sup>[9]</sup>: First, using CNTs instead of  $PdO$  emitter, thus the electron transmission efficiency can be adjusted by controlling the direction of CNTs, theoretical calculations prove that when the angle between CNTs and gate plane reach  $30^\circ$ , almost all electrons can reach the anode and form the emission current; Meanwhile, giving the symmetrical axis of CNT parallel to the gate plane, we can also improve the electron transmission efficiency according to enlarging the relative height between gate and cathode(as shown in Fig. 5).

### 3.2 The structural and theoretical model of the FED's

Fig.5 is a simplified structural model of one FED pixel, in which the emission cathode consists of CNTs, whose symmetrical axis are parallel to the gate and anode planes, supposing the CNT is  $2\mu\text{m}$  long, and closed by a hemisphere with radius  $2.5\text{nm}$  on the top. The distance between anode and gate is  $1.5\text{mm}$ . The side of gate near the CNTs is a quarter arc with radius  $0.05\mu\text{m}$ . By chiral vector, CNTs can be divided into metal and semiconductors which have different band gap. Giving the chiral vectors are uniform distributed, there would be one third of the metal and two thirds of the semiconductor in all type of the carbon tubes <sup>[10]</sup>. But the experimental results of O.Groning<sup>[7]</sup> indicate that CNT's field emission characters fit the theoretical model of metal field emission. The experiments of J.M.Bonard<sup>[11]</sup> demonstrate that, in the case of small current, field emission characters of CNTs fit Fowler-Nordheim formula. So we simplified the CNTs as a metallic cylindrical shell with the end closed by a hemisphere.

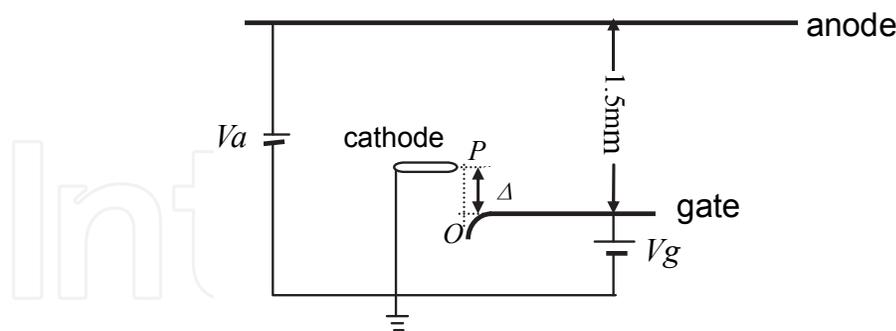


Fig. 5. Model of electric structure

Both the dimension of the electrodes and the distance between them are particularly different (the distance between anode and cathode is 300,000 times than the diameter of CNTs) which brings about the electric field distribution is extremely uneven in the border region, so that the Boundary Element Method (BEM) is an ideal one to calculate the electric distribution on the domain of our interest<sup>[12]</sup>. 106 units are divided on all the electrodes consisting the boundary of one sub-pixel: cathode( CNT), gate and anode. Considering the quite imbalance of charge density distribution in each electrode, especially the charge

density in the cathode is much higher than what in the anode. So that the length of each unit is different in the process of dividing the border, boundary elements tend to put a greater element density where they are needed, such as near the end of electrodes and in regions of high curvature. There are 62 units on the CNTs, 20 units on the gate, and 24 units on the anode. The distribution of initial position, velocity, elevation and intensity of electrons launched by CNT is sampled with Monte Carlo Method.

#### (1). Localization the initial position of electrons

For an electron launched by emitter, how to decide which discrete unit it is from? For given temperature  $T$  and work function  $E_\phi$ , the higher the field intensity, the more probability of electrons can be emitted. According to Fowler-Nordheim formula, the current density emitted from the cathode can be expressed below [13] [14]:

$$J(T) = \frac{4\pi emkTd}{h^3} \exp(-c) \frac{\pi kT / d}{\sin(\pi kT / d)} \quad (3)$$

$$\text{In equation (3), } c = \frac{8\pi\sqrt{2m|E_\phi|^3}}{3he\varepsilon} v(y_0) \quad d = \frac{he\varepsilon}{4\pi\sqrt{2m|E_\phi|} t(y_0)} \quad y_0 = \frac{\sqrt{e^3\varepsilon}}{E_\phi}$$

Where  $e$  is electron charge,  $m$  is electron mass,  $k$  is Boltzman constant,  $h$  is Planck constant,  $\varepsilon$  is electric field strength,  $E_\phi$  is work function of emitter,  $t(y_0)$  is close to 1,  $v(y_0)$  is the Nordheim Function,  $T$  is the temperature of cathode, When equation (3) is normalized, it can be used as emission probability function for cold field emission, so the normalized emission probability density function  $f_1(\varepsilon)$  can be expressed as:

$$f_1(\varepsilon) \approx J(0) / J_M = \frac{1.54 \times 10^{-6} \varepsilon^2}{J_M E_\phi t^2 (e^3 \varepsilon / E_\phi)} \exp[-6.83 \times 10^7 \frac{E_\phi^{3/2}}{\varepsilon} v(y_0)] \quad (4)$$

In equation (4),  $J_M$  is normalized constant. Using expression (4), we can sample the electric density  $\varepsilon$  with Rejection Selection Method [15]. In principle,  $\varepsilon$  can be any value in  $[0, \infty]$ , in order to improve sampling efficiency, we just sample in  $[1.0, \varepsilon_m] \times 10^7$  V/cm. because for cold cathode, the obvious electron emission occurred only when the electric field intensity of emitter surface is up to  $2 \sim 3 \times 10^7$  V/cm, while  $\varepsilon_m$  is the max electric field intensity on CNT's. After sampling a electric field intensity  $\varepsilon$ , a comparison of sampling value is made with all the electric field intensities on the nodes, among which the nearest field intensity of the point is, the node is taken as the emitting position, which serve as the initial position of the traced electrons, furthermore, the electric field intensity of these points can be used to calculate the initial acceleration of electrons.

#### (2) Sampling the initial energies of emitted electrons

The number of electrons with initial energy in  $E \sim E + dE$  is:

$$I(E)dE = \frac{4\pi me}{h^3} \cdot d \cdot \exp(-c) \cdot \frac{\exp[(E - E_F) / d]}{\exp[(E - E_F) / kT] + 1} dE \quad (5)$$

In equation (5),  $E$  is the energy of emitted electron,  $E_F$  is the Fermi energy,  $I(E)$  is the current density with electron energy of  $E$ ,  $I_M$  normalized constant, from equation (5), we can get probability density function  $f_2(E)$  of initial energy below:

$$f_2(E) = \frac{I(E)}{I_M} = \frac{4\pi me}{I_M h^3} \cdot d \cdot \exp(-c) \cdot \frac{\exp[(E - E_F) / d]}{\exp[(E - E_F) / kT] + 1} \quad (6)$$

According to expression (6), we can sample initial energy of electrons with Rejection Selection Method too. Because the energy spectrum of field emission electrons is very narrow [16], the electron energy is in the range of 1.5eV (even just 0.5eV [18]) around Fermi level [16] [17], M. J. Fransen, et al[18] have measured the FWHM of CNTs field emission is 0.11~0.70eV, so we will sample of the emission electrons in 4.8~5.3eV for improving the sampling efficiency.

(3) Elevation angle  $\alpha$  of emitted electrons in each unit obeys Lambert's Law, that is:

$$f_3(\cos \alpha) = \begin{cases} 2 \cos \alpha & 0 < \cos \alpha < 1 \\ 0 & \text{else} \end{cases} \quad (7)$$

From expression (7), we can sample the elevation angle  $\alpha$  of emitted electron.

Assuming  $T=300\text{K}$  in the cathode emitter, the CNT's work function [11] [15] [16]  $E_\phi = 5.0\text{eV}$ ,  $t(y_0) = 1$ . When we completed the sampling of initial position, initial energy and emission direction according with the above steps, the initial state (position, elevation angle, acceleration and velocity) of electrons were completely determined. Then tracing the trajectories of electrons, among them the electrons reached the gate are called the conduction electrons, and those reached the anode called the emission electrons, which eventually bombard the screen to form image information.

### 3.3 The results and analysis

In the calculation process, let anode voltage  $V_a=4000\text{V}$ , gate voltage  $V_g=50\text{V}$ . Fig.6 expresses the electric field intensities of every node on the boundary when the distance  $\Delta$  of CNT's axes above the gate is changed. It is clear that the electric field intensities of CNT's tip can reach strength for field emission; furthermore, the electric field intensity of CNT's tip is three orders of magnitude higher than the electric field intensity on anode. When  $\Delta=0$ , the minimum distance between CNT's apex and gate is 20.7nm. Fig.7 a, b, c and d show that the distributions of electrons reaching the anode with  $\Delta=300\text{nm}$ , 50nm, 5nm, and 0 (assuming in each case, the number of electrons is identical) respectively, while the area under the curve represents the number of electrons reaching the anode. With the increasing of  $\Delta$ , the electron beam has a tendency of dividing into two beams. But on the whole, focusing of electron beam is rather ideal, the smaller  $\Delta$  is, the better it focused. When  $\Delta=5\text{nm}$ , the FWHM of electron beam spot is less than  $50\mu\text{m}$ . With  $\Delta$  changing, the center of the electron beam remains always at about  $100\mu\text{m}$  at the right side of the CNT. This phenomenon must be taken into consideration in the process of the device package.

The relationship of electron transmission efficiency with the vertical distance  $\Delta$  is shown in table 1, when  $\Delta$  decreasing from 300nm to 0, the electron transmission efficiency dropped from 50.5% down to 17%. Therefore, the larger  $\Delta$  is, the less constrain the gate would act to the electrons, which means the more electrons can break the restrain of the gate to reach the anode and form the emission current. Fig.8a shows the changes of the actual total number of electrons (logarithm) emitted at the top of CNT with  $\Delta$  changing. It can be seen that, for both  $\Delta=300\text{nm}$  and  $\Delta=0$ , the total number of electrons emitted from CNTs is 17 orders of magnitude difference, that is to say, if there are two identical CNTs with  $\Delta=300\text{nm}$  and  $\Delta=0$ ,

the field emission of the CNT which is close to the gate will play a decisive role. Fig.8b shows the change of the maximal strength of electric field on CNT's tip with  $\Delta$  changing; No doubt it will directly affect the current density of emission electrons. In fact, in its changing process, the distance between CNT's tip and gate is changing too, so it is difficult to distinguish the main factors whether the vertical distance  $\Delta$  or the transactional distance between CNT's tip and gate that affect the electronic transmission efficiency is. So we can let CNT in two specific position for comparison : in Fig.8, if the arc apex  $O$  on the left of gates is the origin of coordinates, so at two different emitting points  $P_1(0, 100\text{nm})$  and  $P_2(-50\text{nm}, 50\text{nm})$ , in both positions, the distances between the emitting points and gate are all  $61.8\text{nm}$ ., but the electron transmission efficiency are  $44.25\%$  and  $40.75\%$  respectively, and it proves that one can improve the electronic transmission efficiency by increasing  $\Delta$ , compared with the experimental results of Canon corporation [15], we can conclude that even if the CNTs and the gate are in the same plane, the electron transmission efficiency can also be increased only by increasing the transversal distance between cathode and gate, but it needs to increase the voltage of the gate at the same time. In order to test the influence of CNT's angle on the electron transmission efficiency, we set the apex of CNT at coordinate  $(-267.6\text{nm}, 1051.25\text{nm})$  to calculate the transmission efficiencies when the elevation angles equal to  $30^\circ$  and  $0^\circ$ , as a result, the corresponding electron transmission efficiency are  $99.7\%$  and  $64.7\%$  respectively. It shows that the impact of electron emission direction on electronic transmission efficiency is much greater, because the emission electrons have relative high inertia, so there are more electrons can break the strong confinement of the gate and eventually reach the anode.

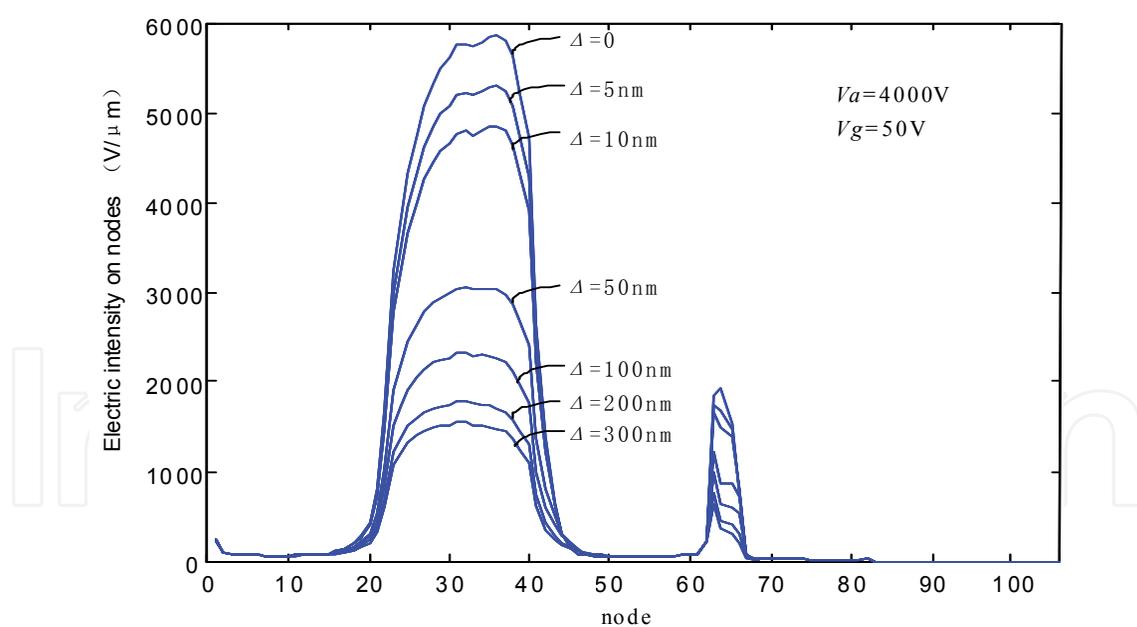


Fig. 6. Relationship of electric intensity on nodes with vertical distance between cathode and gate (the first 62 nodes on tube, the next 20 ones on gate and the last 24 ones on anode)

$\Delta(\text{nm})$	300	200	50	5	0
Efficiency $\eta$ (%)	50.5	45.3	44.25	30.25	17

Table 1. Relationship of electron transmission efficiency with  $\Delta$

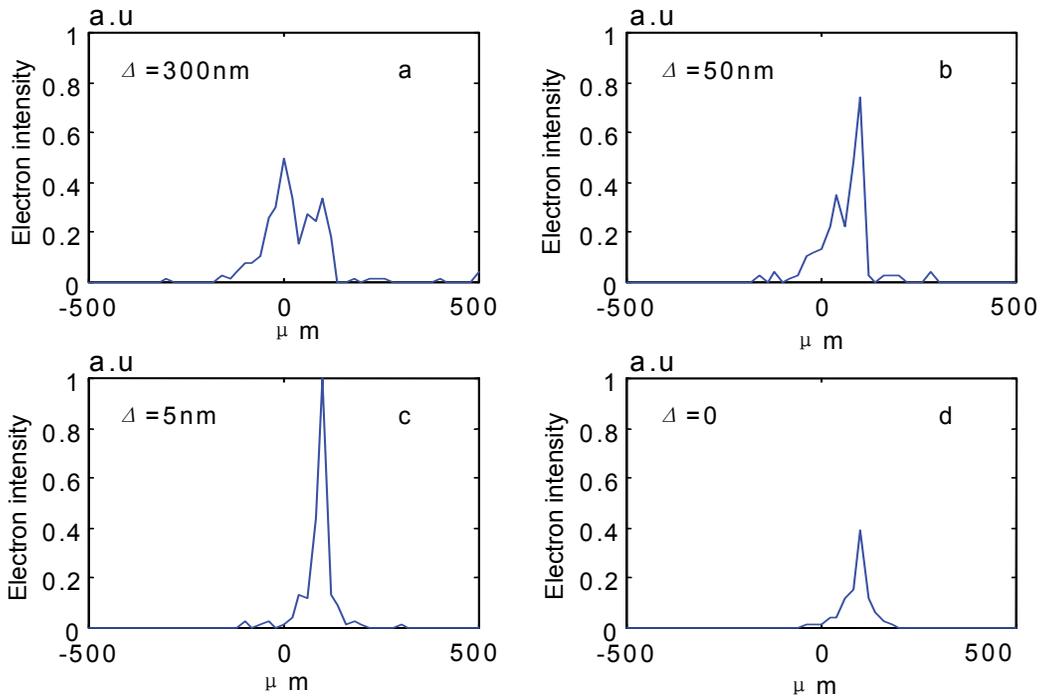


Fig. 7. Distribution of emitted electrons on anode ( $V_a=4000V$ ,  $V_g=50V$ , X axis representing the X coordinate of emitted electrons, ranged from  $-500$  to  $500\mu m$ )

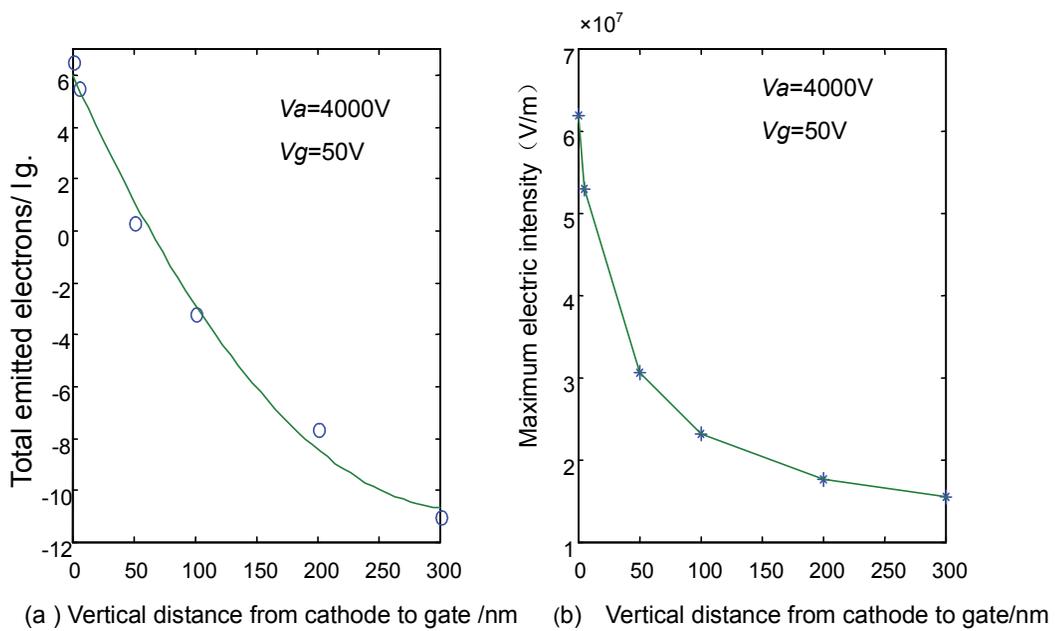


Fig. 8. (a) Relationship of total emitted electrons with the vertical distance  $\Delta$  (b) Relationship of maximum electric intensity on cathode with  $\Delta$

### 3.4 Conclusion

Although the driving voltage of the FED with surface conduction of the Canon corporation is lower (12V), but the distance between cathode and gate is just about 10nm, resulting in the lower electron transmission efficiency, thus limiting the brightness of the display. By increasing the distance between the cathode and gate and the relative height between cathode and gate, especially increasing the elevation angle of CNTs, one can substantially improve the electron transmission efficiency. On the other hand, the focusing performance of electrons reaching anode would be worse, and the gate voltage has to increase, so that we must make an appropriate choice among electron transmission efficiency, driving voltage, resolution and simple arts and crafts.

## 4. Design and experiment on a field emission display prototype based on CNTs

### 4.1 The main points and technical background

Display devices based on carbon materials are considered to be the best choice for field emission large area displays (40" diagonal or larger). CNTs are capable of emitting high currents (up to 1 A/cm<sup>2</sup>) at low fields ( $\sim 5\text{V}/\mu\text{m}$ ) [16], and are believed to be ideal candidates for the next generation of field emission flat panel displays and lighting elements. Choi<sup>[17]</sup> *et al* have demonstrated a fully sealed 4.5 in diode field-emission display using single-wall CNT organic binder. In order to use CNTs as the electron field emitters for large-area displays, it is desirable that an inexpensive substrate such as a lime glass plate can be used for CNTs deposition. A patterned conductive layer needs to be formed on a glass plate before CNT is coated onto the substrate and used as electrode lines. Because of the low melting point of glass and the large mismatch in the coefficient of thermal expansion between metal and glass, carbon deposition cannot be performed at too high a temperature. Previous efforts have been concentrated on controlling the growth process to produce arrays of aligned CNT on patterned substrates and have been successful in some aspects<sup>[18-21]</sup>. At the same time, various low temperature chemical vapor deposition (CVD) techniques are being studied to achieve low threshold field emission of electrons at a high emission current density<sup>[22][23]</sup>. Vertically aligned CNTs have been synthesized by plasma-enhanced CVD<sup>[1]</sup>.

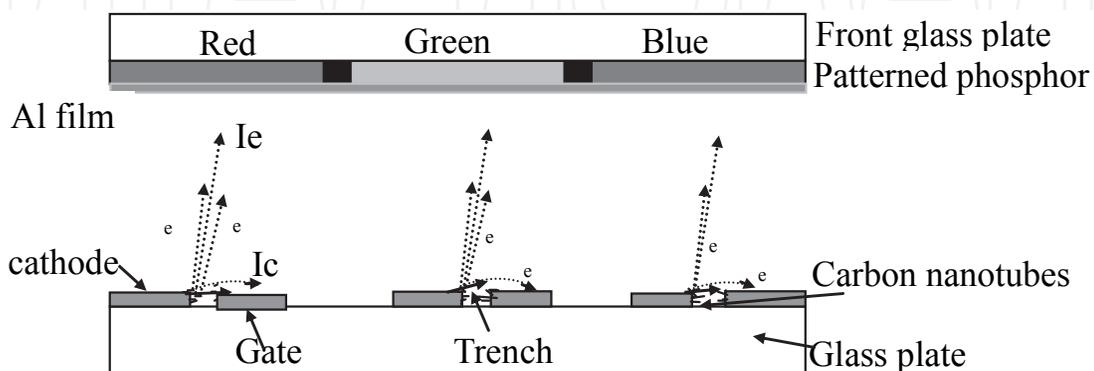


Fig. 9. Schematic structure of a pixel of the flat panel display

Nevertheless, control of a large area synthesis is not easily accessible with such approaches, because this technique requires methods such as e-beam lithography to produce patterned catalyst that is time consuming and expensive for large devices. On the other hand, the complexity of manufacturing gate electrode either on top or beneath of the cathode is unendurable, especially the rigorous requirement of uniform for both the radii of emitter tips and the gate holes, which blocked the development of traditional triode FED. One more efficient way of producing CNT field emission devices is mixing CNT with metal nanoparticles in epoxy, results indicate that aligning CNT with the polymer matrix is unnecessary, and the field emission properties comparable to those of aligned CNT can be enduring.

In this part we propose a new type of triode FED prototype that the field emitters are fabricated with CNT organic binders, seeing that the cathode and gate electrode are on the same base plate, this type of FED is easily scalable, and the man stages can be more simplified compared with traditional ones. Besides, it has a high electron transmission ratio of 29.3%, which is well consistent with the results of our theoretical simulation. The proposed triode structure of display is more simple in its fabrication process compared with traditional ones. Our FED prototype possesses a series of good performances such as outstanding brightness, low power consumption et al.

#### 4.2 Experiment description

In our experiment, the panel structure of FE-flat panel display is designed as shown in Fig. 9, there are two sets of glass plates: front plate and base plate, CNT binder is between the patterned cathode and gate electrodes on the base plate, and phosphor-coated Al film is on the front glass. The distance between two sets of glass plates is about 1mm, each pixel includes three sub-pixels to realize full color display. The manufacture arts include: firstly, after thoroughly cleaning the substrate with pure water and organic solvent, a pair of device electrodes is formed on the insulating substrate by a proper means, such as vacuum deposition or photolithography; secondly, longitudinal and transverse metal stripes (which are kept insulated with SiO<sub>2</sub> at the cross part) are formed to link the device electrodes respectively, thus a series of matrix configuration ( pixel) is formed; thirdly, after the CNT polymer is silk screened between the device electrodes, the polymer was heated at 300°C to 400°C for a little more than 10 minutes, when the organic components are removed, the binder can have a high conductivity to provide electrons to the emitters incessantly, at last, we etch a trench in the middle of the CNT paste with laser beam(YAG). We can see clearly that CNTs are kept on the edge of trench while the nickel nano-particles are melted (see Fig.10b), resulting from their different melting points, and no other than these CNTs consist the virtual emitters. The scanning electron micrograph (SEM) image indicated that not only the slope angles and lengths of CNTs on the edge of trench are not the same, but the CNTs density at different area along the trench is also not uniform. All the factors above can lead the light dots on screen very different, of both its brightness and size. When the density of CNTs reached to certain numbers, the light dots should connect together in a bright line. The trench width is about 0.05mm to 0.37mm depending on the thickness of paste and the diameter and power of laser beam, in our experiment, the trench width is about 200μm, and CNTs diameters are distributed from 20 nm to 40 nm.

The experiments are conducted in a vacuum chamber with the pressure level of  $1 \times 10^{-3}$  Pa. Fig.11 shows the light spots at different anode voltage above the trench, all the light spots are arranged on a line except the top right one, which is the emitting of CNTs on a protuberance formed when pull up the silk screen, only the voltage on anode is high enough to produce electron emitting. in order to confirm this, we reduced the voltage on gate electrode down to zero and found that all the light spots arranged on a line disappeared while the spot on top right existing. In this point, the electro-conductive stripe can also be made with CNT paste as long as the stripe surface is smooth enough, only the voltage on the anode is not high enough to pull out electrons from CNTs on upside of the stripe surface.

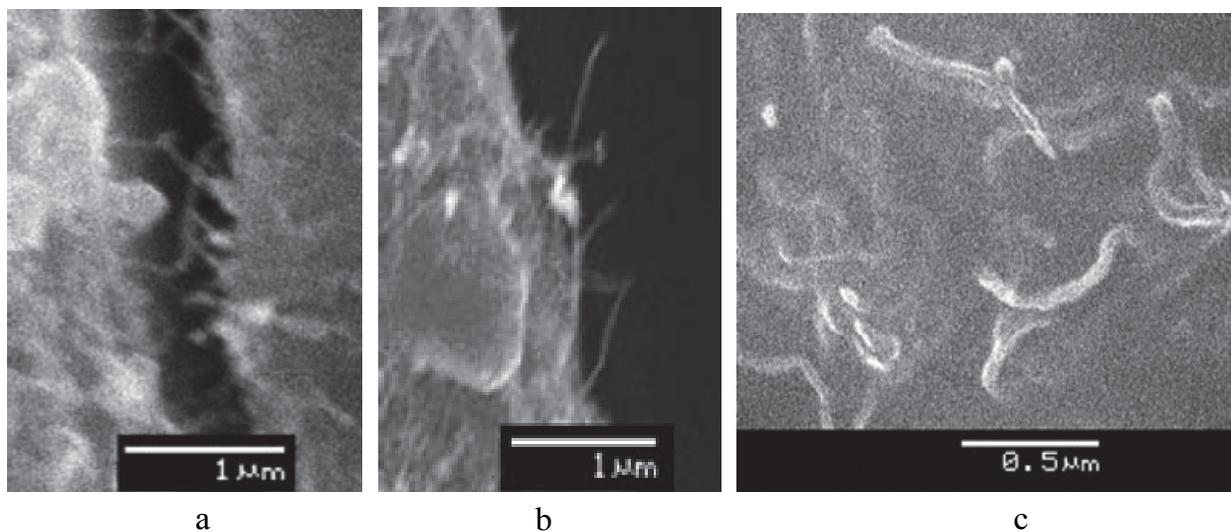


Fig. 10. Nanotubes on the trench: a). Nanotubes on both edge a trench formed by cool shrink b). Nanotubes on a trench etched by laser beam c). Nanotubes on the binder surface

Fig. 11 shows the light spots on screen with anode voltage equal to 2.8kV, 2.9kV, 3.0kV and 3.2kV respectively, while the gate voltage keep on 380V. From the emission display we can see that the higher the anode voltage is, the more CNTs take part in emitting electrons and the more electrons reach to anode, therefore, giving higher emission efficiency. In Fig.15c, the total emitting current from CNTs ( $I_c$ ) on the edge of trench is  $1.1 \mu\text{A}$ , the emission current arrived at anode ( $I_e$ ) is  $0.33 \mu\text{A}$ , the emission current ( $I_s$ ) from CNTs on the protuberance is  $0.01 \mu\text{A}$  when the gate voltage is reduced to 0, so the electron transmission ratio:  $\eta = (I_e - I_s) / I_c = 29.3\%$ , which is much higher than that of Canon Corporation [24]. In fact, our previous simulation with Monte Carlo method and Boundary Element method has demonstrated that when the slope angle of CNT improves to 30 degree, almost all electrons can reach to anode, which implies a higher electron transmission ratio [25]. Fig. 12 a) shows emission current of CNTs as a function of electric voltage. Fig.12 b) is corresponding to Fowler–Nordheim (F–N) plot of CNTs, indicating a conventional field-emission mechanism. The emission current

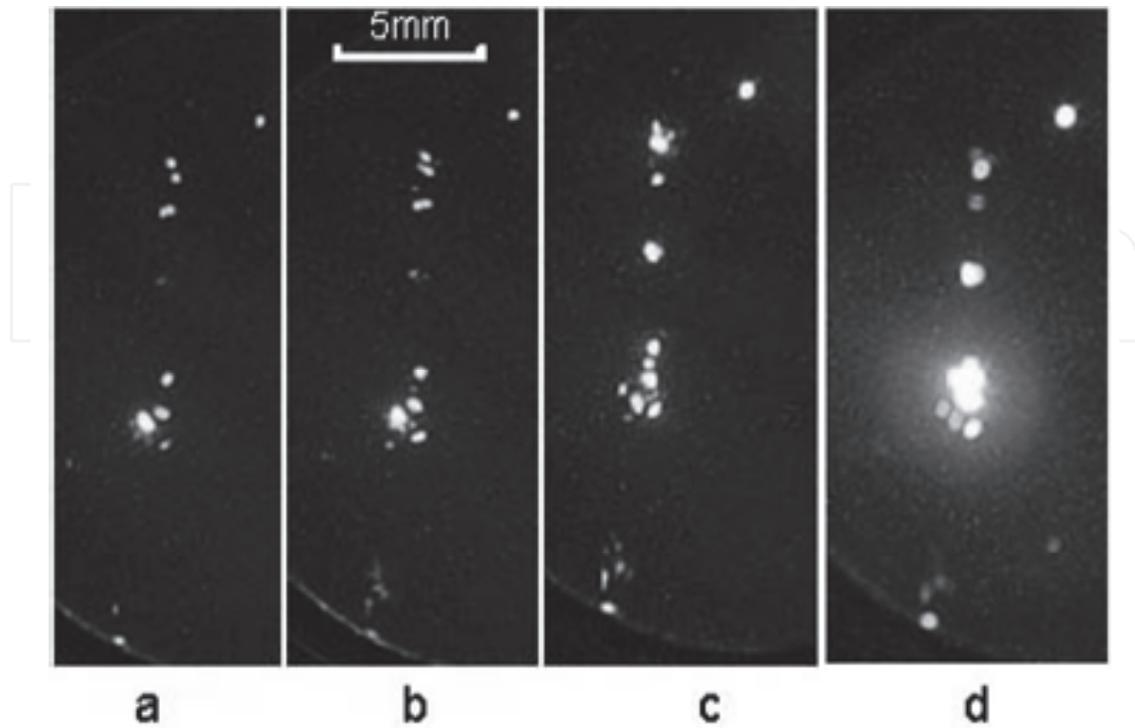


Fig. 11. a, b, c, d are light spots on the screen with different anode voltages 2.8KV, 2.9 KV, 3.0 KV, 3.2 KV respectively(voltage on gate is  $V_g=380v$ ), The cathode current  $I_c=1.1\mu A$  and the anode current  $I_e=0.33\mu A$  in Fig17c

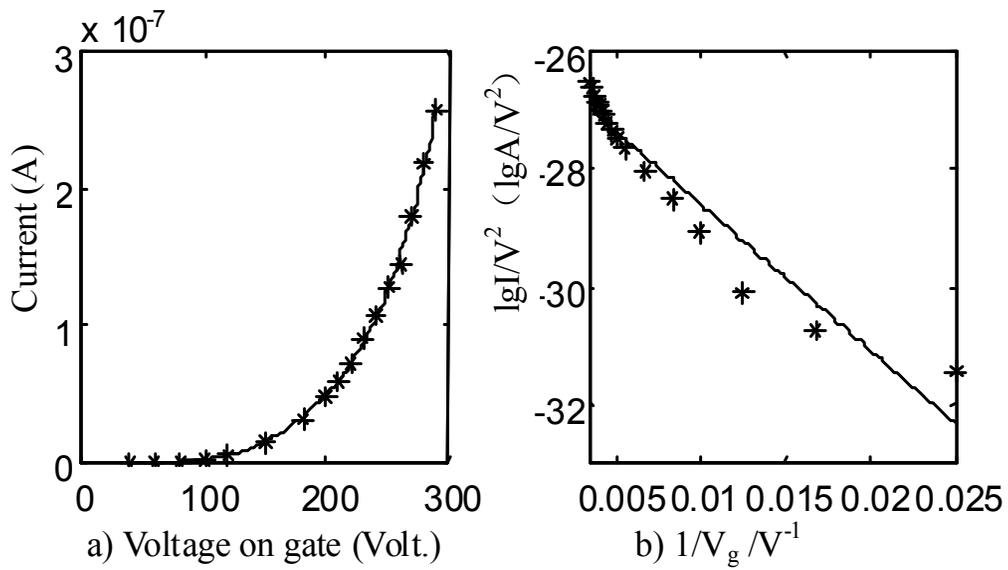


Fig. 12. I-V curve and F-N plot

significantly deviated from F-N behavior in the high-field region, which, we have given a reasonable explanation in other article [26]. We also observed the emission stability of CNTs along trench edge, keeping the voltages on anode and gate fixed, both the total current ( $I_c$ ) and the emitting current ( $I_e$ ) are very stable, and the current fluctuation is not excess to 3% during our one hour's observation.

In summary, a large area, fully colored field emission display panel prototype based upon carbon-CNT emitters was proposed in this research, and there is still a lot of work to do: In our experiment, the trench edge is very irregular, yet the length of CNTs, the wide trench (about 0.2mm) leads to a high gate voltage (380V), the distributing uniformity of CNTs also needs to be improved. We can use a smaller-diameter laser beam to etch CNT paste and before mixing the CNTs by cutting short with chemical or physical methods. To further reduce the gate voltage, single walled CNTs is advisable. To our delight, C.H. Poal<sup>[27]</sup> et al have mixed high quality single-walled CNT paste suitable for our application. When all these obstacles are removed, we will get higher image quality and lower gate voltages.

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## **Carbon Nanotubes - Synthesis, Characterization, Applications**

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Carbon nanotubes are one of the most intriguing new materials with extraordinary properties being discovered in the last decade. The unique structure of carbon nanotubes provides nanotubes with extraordinary mechanical and electrical properties. The outstanding properties that these materials possess have opened new interesting researches areas in nanoscience and nanotechnology. Although nanotubes are very promising in a wide variety of fields, application of individual nanotubes for large scale production has been limited. The main roadblocks, which hinder its use, are limited understanding of its synthesis and electrical properties which lead to difficulty in structure control, existence of impurities, and poor processability. This book makes an attempt to provide indepth study and analysis of various synthesis methods, processing techniques and characterization of carbon nanotubes that will lead to the increased applications of carbon nanotubes.

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