Chapter 7

Fabrication and Characterization of lateral Field Emission Device of Carbon Nanotubes

We have proposed and fabricated a vertical lateral field emission device (LFED) of carbon nanotubes (CNTs). It combines high-performance nano-materials with mature solid-state fabrication technology to produce miniaturized vacuum devices with superior field emission characteristics. The techniques employed are very simple and allow for good reproducibility in controlling the short distance from the polysilicon anode to the CNTs cathode inter-electrode distance. The inter-electrode gap can be easily fabricated to be less than 1 μm by a wet etching process without using fine lithography. The CNTs were selectively grown using a microwave-plasma enhanced chemical vapor deposition system (MPCVD). The anode-to-emitter gap distance and the length of carbon nanotubes are well controlled to enable investigation of their effect on the field emission properties. The turn–on voltage of the fabricated device with an inter-electrode gap of 0.53 um is as low as 0.2 V, and the emission current is as high as 9.72 mA at 10 V. The emission current fluctuation is approximately ± 3.5% for 1500s .

7.1 Introduction

Recently, there has been enormous interest in vacuum field emitters because of their great tolerance to high-temperature and high-radiation environments [7.1-7.2]. The potential applications of vacuum microelectronics include field emission displays, microwave power amplifiers, scanning tunneling microscopes, and microsized intense electron sources [7.3-7.6]. Their operation is based on the high-electric-field-induced transfer of electrons through a vacuum from a cathode to an anode.

LFED with Si or metal tips have been demonstrated**;** they have many advantages, such as a low turn-on voltage, high current densities, and high transconductance. However, lateral field emission devices have poor emission site densities**;** they require complicated processes to produce high emission current site densities [7.7-7.12]. In order to achieve high electron emission current at low applied voltage, it is necessary to produce fine sharp features and/or use low-work-function materials for cold-cathode operation. As field emitters, carbon nanotubes (CNTs) exhibit excellent field emission characteristics due to their high aspect ratios, small tip radii of curvature, high chemical stability, and high mechanical strength [7.13-7.18]. A low turn-on electric field of 0.8 V/μm [7.19] and a high emission current density of 80mA/cm^2 have been reported [7.20] for CNT field emitters. . In addition, the structure of a lateral field emission device has little overlap between the two

electrodes, and thus it has a low parasitic capacitance; therefore, a lateral field emission vacuum diode is suitable for high-speed operation.

The triode structure is for display applications. The CNT cathode, gate electrode and anode in our I-V measurement system are the three electrodes. The CNT cathode and gate electrode are fabricated for our device. Because the large leakage current to the gate electrode from the CNT cathode due to a short gate-cathode distance results in a large electric field, we use the same structure and operation as for a lateral field emission diode rather than that of a triode structure. We apply a voltage between the gate and the CNT cathode and measure the current between them. It is clear that we can achieve a large lateral field emission current by shortening the gate to cathode distance. Therefore, the large gate leakage current is simply the current measured in our lateral field emission diode. For conventional diode operation, we refer to the anode instead of the gate electrode, and the CNT is treated as the cathode in this discussion.

Therefore, the goal for this device is to achieve low turn-on voltage, high-speed operation, high field emission current density and low parasitic capacitance for lateral field emission vacuum diodes based on carbon nanotubes by simple fabrication and precise control of electrodes without fine lithography. In this report, the CNTs were selectively grown by microwave plasma enhanced chemical vapor deposition

(MPCVD). The anode-to-emitter gap distance and the length of CNTs were well controlled to enable the investigation of their effect on the field emission properties. Ultralow turn–on voltage (approximately 0.2 V) and high lateral field emission current (about 9.72 mA and 3.9 A/cm^2 for the given current density) were obtained with an inter-electrode gap of 0.53 μm. The emission current fluctuation was also studied over a short term period of 1500 s. No obvious degradation of emission current was observed, and the fluctuation was approximately ±3.5%.

7.2 Experimental Procedures

The fabrication procedure of the CNT lateral field emission device is shown schematically in Figs. 7.1(a) – 7.1(e). As shown in Fig. 7.1(a), initially, a 500-nm-thick thermal oxide layer was growth on an N-type Si(100) substrate at 1050 ℃. A 200-nm-thick poly-Si layer was then deposited on the thermal oxide layer by low- pressure chemical vapor deposition (LPCVD) using pure precursor SiH_4 at 620 ℃. The poly Si was further doped with phosphorous using a solid diffusion source (PH-1000N) at 950℃ for 25 min after which phosphorous was driven in at 950℃ for 20 min. The sheet resistance of poly Si was 40 Ω/□ measured using a 4-point probe. A 1-um-thick photoresist was spin-coated on the poly-Si layer and an array of 50×50 square patterns, each 10 μm long, (the emission area was 25x10^{-4} cm^2) over a 1 mm x

1 mm was defined by photolithography. Afterward, the poly Si layer was dry etched by the inductive coupled plasma reactive ion etcher (ICP-RIE), and the SiO_2 layer was laterally etched in a wet etching solution of buffered oxide etch (BOE) with the etching time precisely controlled, as shown in Fig.7.1(b). Then, the poly-Si layer was continuously laterally etched with a wet etching solution of poly etcher. With a precisely controlled lateral etching time, we easily fabricated an inter-electrode gap less than 1 μm. A 3.5-nm-thick iron layer, to serve as the catalyst, was deposited directly onto the photoresist-patterned Si substrate by electron beam evaporation, and the square iron patterns were transferred to the silicon substrate after the photoresist was removed by the lift-off method as depicted in Figs.7.1(c) and 7.1(d). Finally, as depicted in Fig. 7.1(e), CNTs were selectively grown on the iron layers by microwave plasma-enhanced CVD. CH_4, N_2 and H_2 were used as the source gases, and their flow rates were 10, 80 and 80 sccm, respectively. The microwave power was maintained at 1.2 kW and the chamber pressure was set at 35 Torr. The substrate temperature was estimated to be approximately 800℃ and the deposition time was 20 min.

The growth morphology of CNTs was observed by scanning electron microscopy (SEM) and the field emission properties of lateral CNT diodes were measured in a high-vacuum environment with a base pressure of 1.0×10^{-6}Torr. During the measurement, the device was in a grounded emitter configuration. Before

the electrical measurement, a constant voltage of 10 V was applied to the poly-Si for 10 min. to exhaust adsorbed molecules. A voltage swept from -10 V to 10 V was applied to the anode to obtain the current-voltage characteristics of the vertical CNT lateral field emission diode. Both the anode and emitter currents were measured as functions of anode-to-cathode bias voltage using Keithley 237 high-voltage units with an IEEE 488 interface controlled using a personal computer.

7.3 Results and Discussion

7.3.1 Effect of anode-to-emitter gap

The SEM micrograph of the fabricated CNT LFED for a SiO_2 lateral etching time of 16 min is shown in Fig. 7.2(a). The CNTs were selectively grown on the catalyst metal within the cathode region. It can be seen that CNTs are uniformly distributed and few carbonaceous particles are observed. Figure 7.2(b) shows a cross-sectional SEM micrograph of the vertical CNT LFED. The average height of the CNTs is approximately 2.6 μm and the gap between the anode and CNTs is 1.84 μm. The gap between the anode and CNTs can be controlled by varying the SiO_2 lateral etching time. Figure 7.3 shows SEM micrographs of the vertical CNT LFED for a SiO_2 lateral etching time of 7 min. The growth time of the CNTs was also 20 min. The gap between the gate and CNTs can be further reduced to 0.53 μm.

Figure 7.4(a) shows the emission current-voltage characteristics of vertical CNT LFEDs with different anode-to-emitter gaps. The emission currents (I_a) were measured as a function of anode voltage (V_a) swept from negative voltage to positive voltage. The voltage-current characteristics show a good rectification. The turn-on voltages (V_{on}) defined where the F-N plot becomes linear were 0.2 V and 0.5 V for anode-to-emitter gaps of 0.53 μm and 1.84 μm, respectively. Low turn-on voltages were achieved for these vertical CNT LFEDs. Emission currenta of 9.72 mA and 4.3 mA were obtained at an anode voltage of 10 V for anode-to-emitter gaps of 0.53 μm and 1.84 μm, respectively. The anode operation voltage can be significantly reduced by decreasing the anode-to-emitter gap. The Fowler-Nordheim plot of the emission current is shown in Fig. 7.4(b). The linearity clearly indicates the confirmation of the field emission phenomenon. From Fig. 7.4(b), we also find that the slope in the case of the 0.53 μm anode-to-emitter gap is smaller than that of the 1.84 μm case. According to Fowler-Nordhiem tunneling, the local field enhancement factor is inversely proportional to the slope of the F-N plot. Therefore, we can achieve a large electric field at a small anode voltage by reducing the anode-to-emitter gap to prduce higher local field enhancement factor (β) value. A low turn-on voltage and higher lateral field emission current can thus be obtained with a shorter anode-cathode distance by controlling the SiO_2 lateral etching time. This is much simpler than the

conventional methods.

7.3.2 Effect of the length of CNTs

The effect of the length of CNTs on field emission properties was investigated with the anode-to-emitter gap maintained at approximately1.9 μm. The length of CNTs can be controlled by changing the growth time. Figures 7.5(a) -7.5(c) show cross-sectional SEM micrographs of vertical CNT LFEDs for the growth times of 3 min, 10 min, and 20 min, respectively. The lengths of the CNTs are 0.2 μm, 0.6 μm, and 2.46 μm for the growth times of 3 min, 10 min, and 20 min, respectively. The tops of the CNTs for the growth time of 20 min are higher than the anode and those for the growth time of 3 min are lower than the anode. The tops of CNTs for the growth time of 10 min are approximately the same height as the anode. Uniform growth of CNTs was achieved over the entire array for all CNT LFEDs.

The lateral field emission current-voltage I_a vs V_a characteristics of vertical CNT LFED for different lengths of CNTs are shown in Fig. 7.6(a). The turn-on voltages are 1 V, 0.4 V, and 0.5 V for the lengths of 0.26 μm, 0.6 μm, and 2.46 μm, respectively. Moreover, at an anode voltage of 10 V, lateral emission currents of 0.5 mA , 2.1 mA and 4.5 mA can be achieved for lengths of 0.26 μm, 0.6 μm, and 2.46 μm, respectively. In the case of CNTs 0.26 μm long, a higher turn-on voltage is required

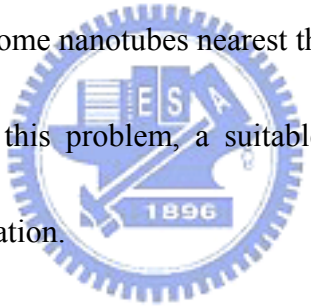
for nanotubes lower than the top of the anode. This is ascribed to the larger distance between the anode and CNTs requiring a larger electrical field to cause the CNTs to emit electrons. Therefore, the lateral emission current is also the lowest among the above three cases at an anode voltage of 10 V. However, in the case of CNTs 2.6 μm long, the lateral emission current is the largest in the above three cases and the low turn-on voltage almost equals that for the case of CNTs 0.6 μm long. This lowest turn-on voltage is thought to be due to the shortest distance between the anode and the CNTs. Possible explanations for this result are as follows. Carbon nanotubes are likely to flex to orient themselves toward the anode under higher electric fields [21] , so that the real distance between anode and emitter becomes shorter even though the CNTs are much higher than the the top of the anode; therefore, the electric field becomes larger and allows the CNTs to emit more electrons at a lower anode voltage. This is also why the low turn-on voltage in the case with CNTs 2.6 μm long is almost equal to that in the case with CNTs 0.6 μm long. As for the highest lateral field emission current for the case of 2.6 μm-long CNTs, a possible explanation is that there are a large number of structural defects existing on the surface of the nanotubes as well as on their tips. These defects serve as emission sites to increase the total emission current. Chen *et al.*[22] previously reported that the field emission from nanotubes would be comprehensive from the tube tip and body. The small radius of the tube wall

and the existence of defects are suggested as the reasons for the emission of electrons from the body of the tubes. The corresponding F-N plots of the vertical CNT LFED for different lengths of nanotubes are shown in Fig. 7.6(b). The linearity confirms the field emission property of the fabricated devices. If CNTs are so long that they bend toward the anode under high positive voltage, a short circuit between the CNTs and the anode is likely to occur and the emission current will be different for different measurements. Figure 7.7 depicts the results of the reliability measurements for the field emission current of the CNTs. The case of CNT growth time of 20 min shows poor reliability of emission current after several measurements. A possible explanation is that the CNTs are likely to flex to orient themselves toward the anode under higher electric fields. Some CNTs which were closest to the anode were permanently deformed after several measurements and burned out due to short circuits to the anode. Then, the next preferable CNT emitters, which have a larger distance to the anode and thus have a lower field enhanced factor, would require a higher electric field; therefore, the turn-on voltage is increased and the field emission current is reduced at the same anode voltage.

7.3.3 Breakdown phenomenon and emission sites of CNTs

Figure 7.8 shows the breakdown phenomenon of a LFED with CNTs 0.6 um

long. The field emission current degraded from 6 mA to 100 μA under an applied voltage of 20 V. The degradation of emission current is attributed to a decrease in the number of effective emission sites of CNTs resulting from the high emission current under high electrical field. Some emitter CNTs are burned out due to the joule heat caused by the high emission current, and some emitter CNTs probably fly away under strong electrical fields due to poor adhesion between the nanotubes and the substrate. A damaged device requires a higher turn-on electric field because the next preferable CNT emitters have a larger distance between themselves and the anode. Figure 7.9 shows the damage observed; some nanotubes nearest the anode disappeared due to the high electric field. To avoid this problem, a suitable current limitation should be considered during device operation.



7.3.4 Stability of Field Emission Current

The emission current stability test was performed on the CNT LFED. An average emission current (I_0) of 0.26 mA was established at an anode voltage of 5 V with the cathode grounded. The emission current reliability over a short period of 1500 s is shown in Fig. 7.10. No obvious degradation of emission current was observed, and the fluctuation was approximately ±3.5%.

7.4 Conclusions

Based on the selective growth of CNTs via MPCVD, a vertical CNT LFED was proposed for the first time. The distance between the poly-silicon collector and the CNT emitter was determined by the wet etching process. Thus, the inter-electrode gap is easily formed with good uniformity and reproducibility at dimensions below 1 μm. The turn–on voltage of the fabricated device with an inter-electrode gap of 0.53 μm is as low as 0.2 V, and the emission current density is as high as 9.72 mA at 10 volt. We also observed the effect of the length of CNTs on the lateral field emission. The larger the distance between anode and CNTs, the higher the applied voltage required. We obtained 10.8 mA lateral field emission current with the anode-to-emitter gap maintained at approximately 1.9 μm and with CNTs 2.46 μm in length. The emission current fluctuation was approximately ± 3.5% for1500 s.

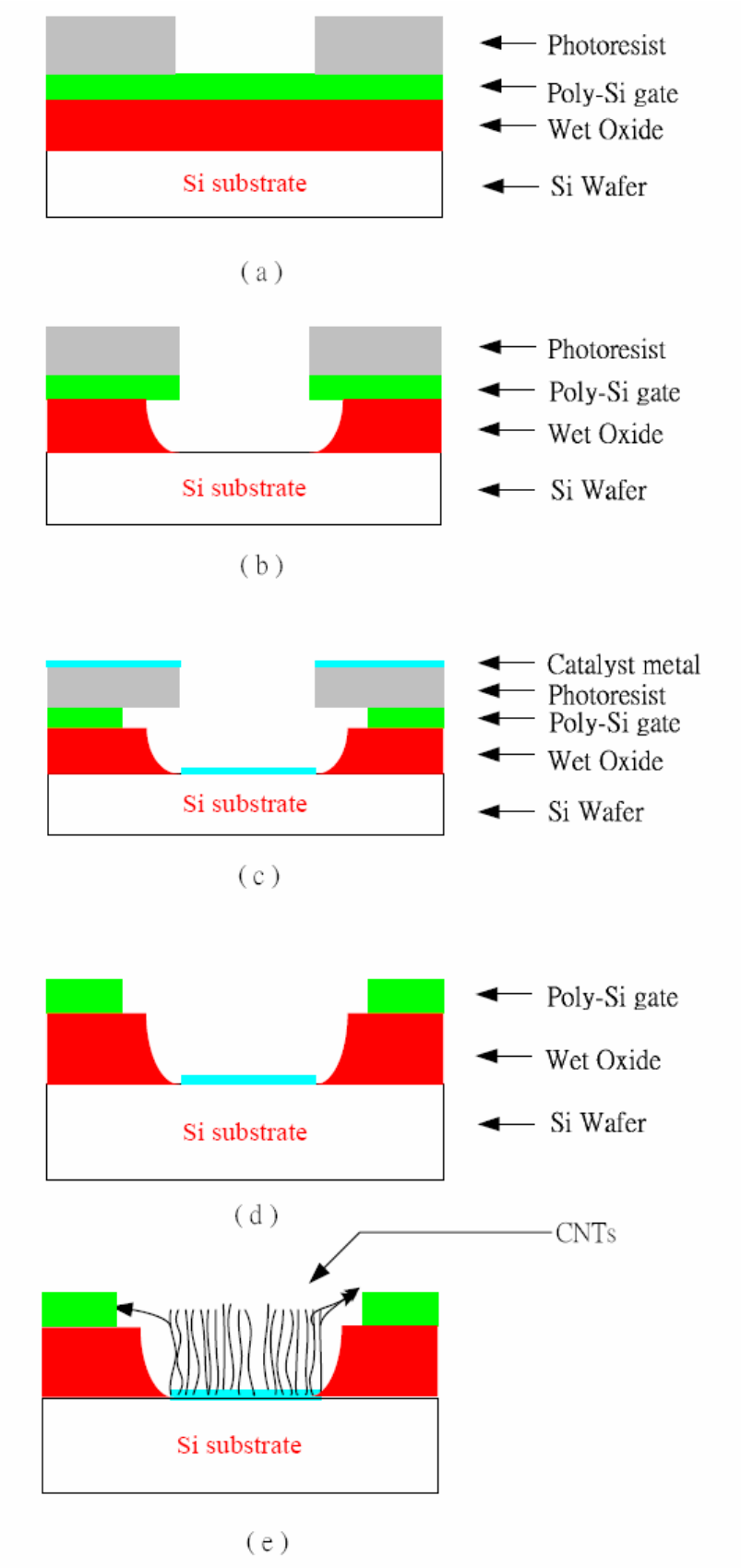
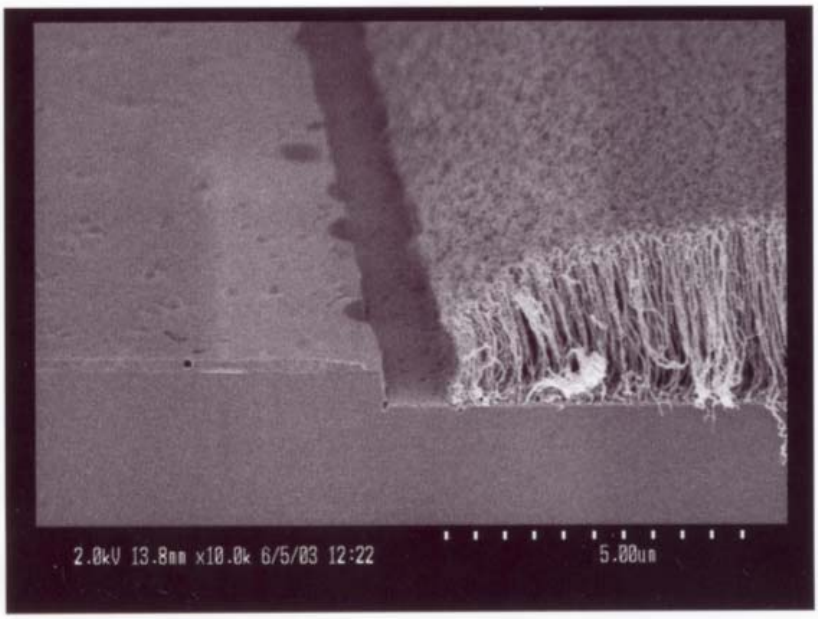
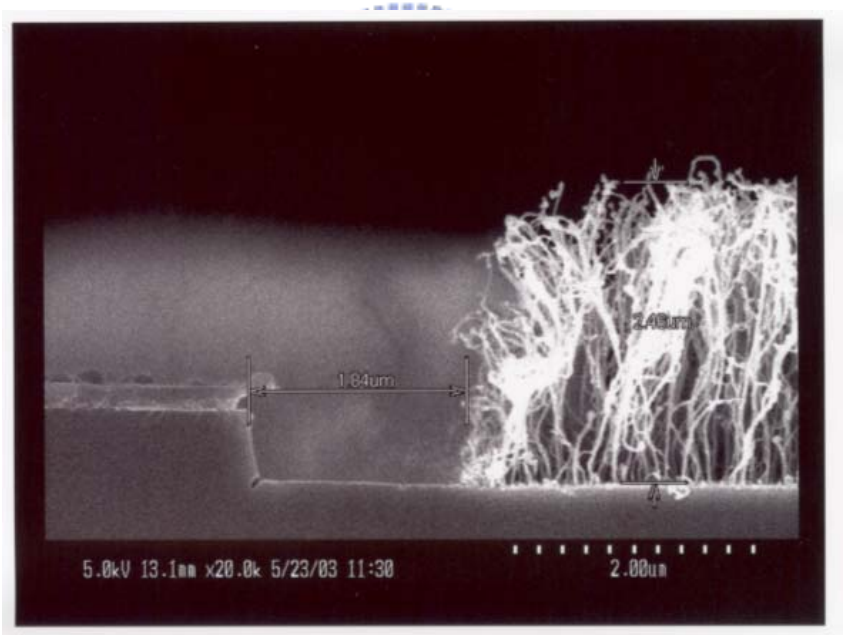


Figure 7-1 Schematic of fabrication procedures for vertical CNT LFED

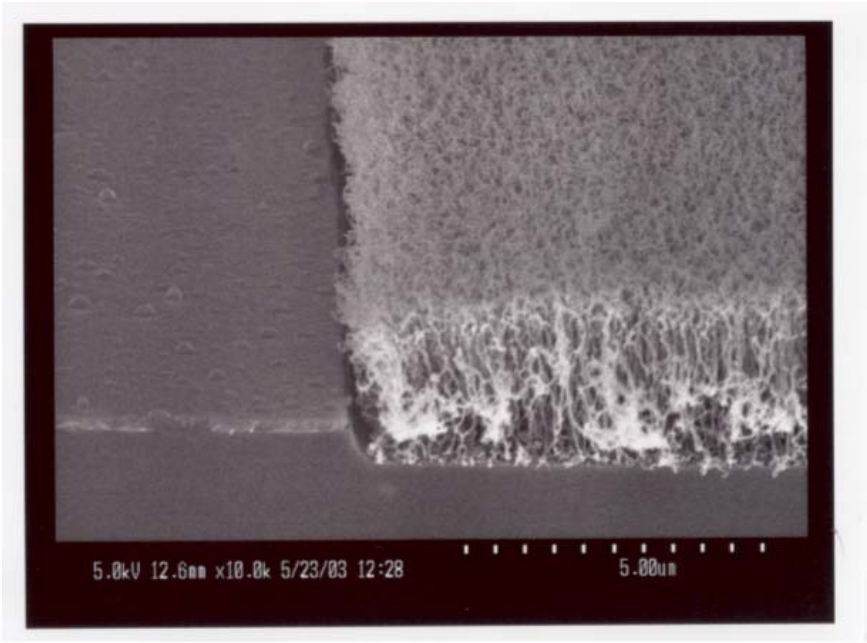


(a)



(b)

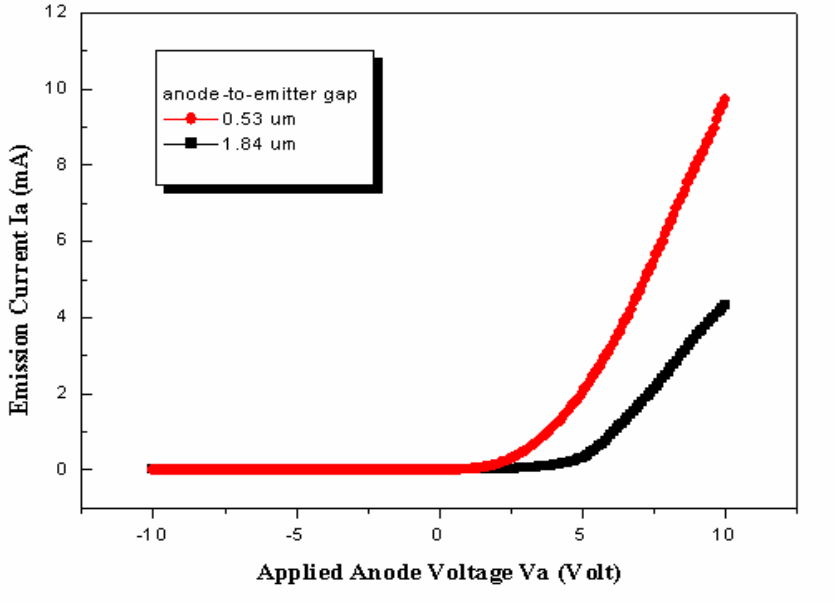
Figure 7-2 (a) SEM micrograph of vertical CNT LFED for SiO_2 lateral etching time of 16 min. (b) Cross-sectional SEM micrograph of CNT diode showing anode-to-emitter gap of 1.84 μm.



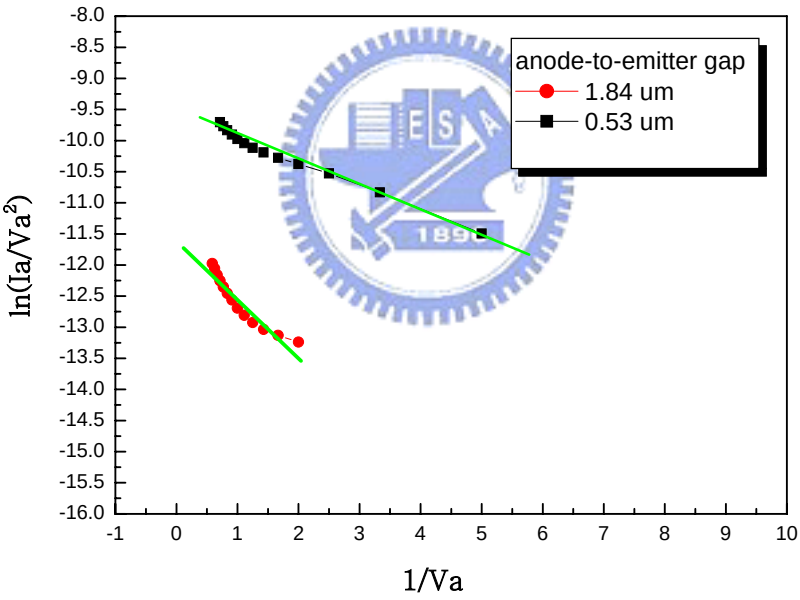
(a)

(b)

Figure 7-3 (a) SEM micrograph of vertical CNT LFED for SiO_2 lateral etching time of 7 min. (b) Cross-sectional SEM micrograph of CNT diode showing anode-to-emitter gap of 0.53 μm.

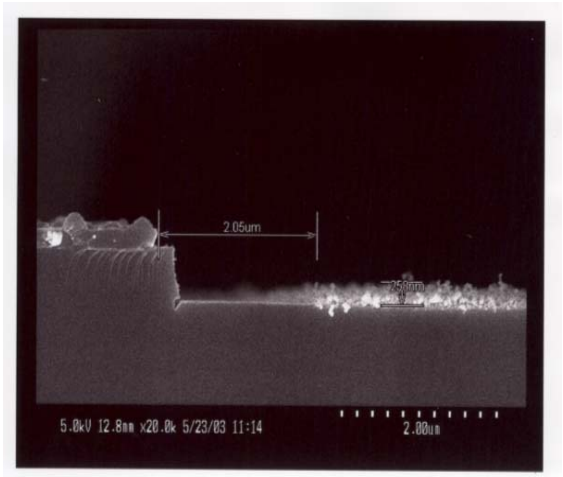


(a)

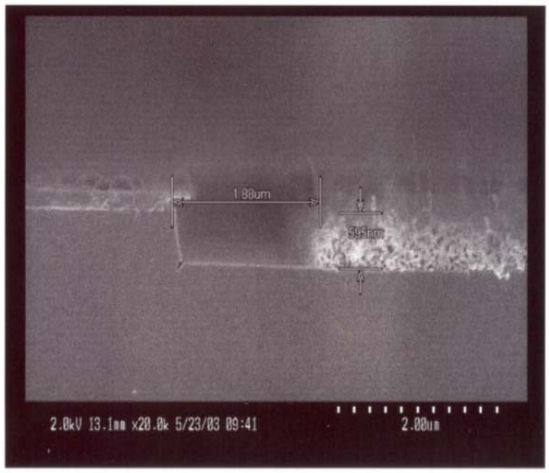


(b)

Figure 7-4 (a) Emission current (I_a) and anode voltage (V_a) characteristics of vertical CNT LFED for different anode-to-emitter gaps, and (b) corresponding F-N plots.



(a)



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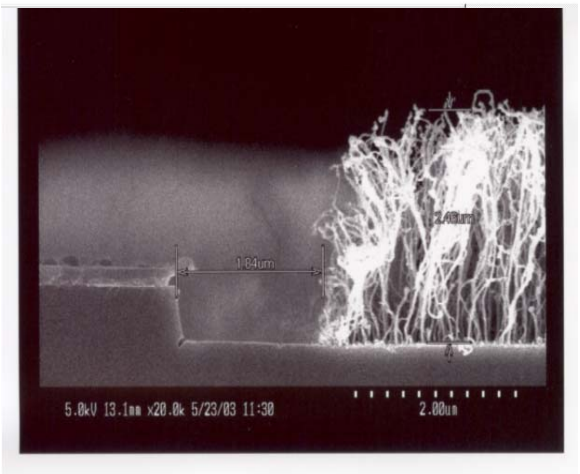
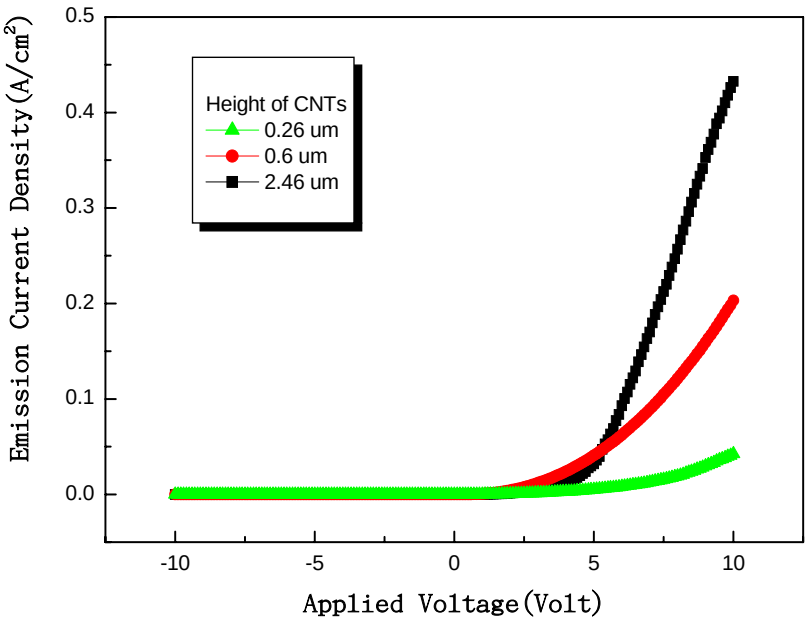
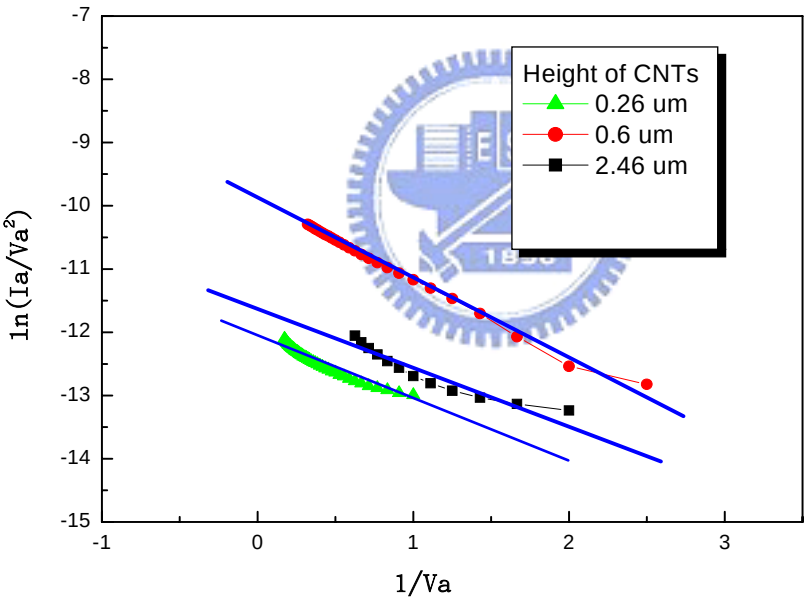


(c)

Figure 7-5 Cross-sectional SEM micrographs of vertical CNT LFED showing different CNT lengths: (a) 0.26 μm, (b) 0.6 μm, and (c) 2.46 μm .

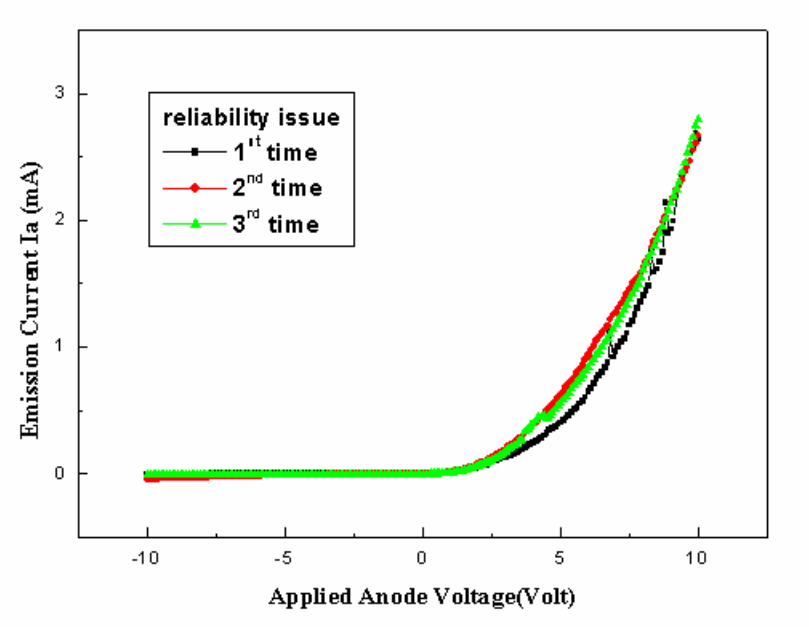


(a)

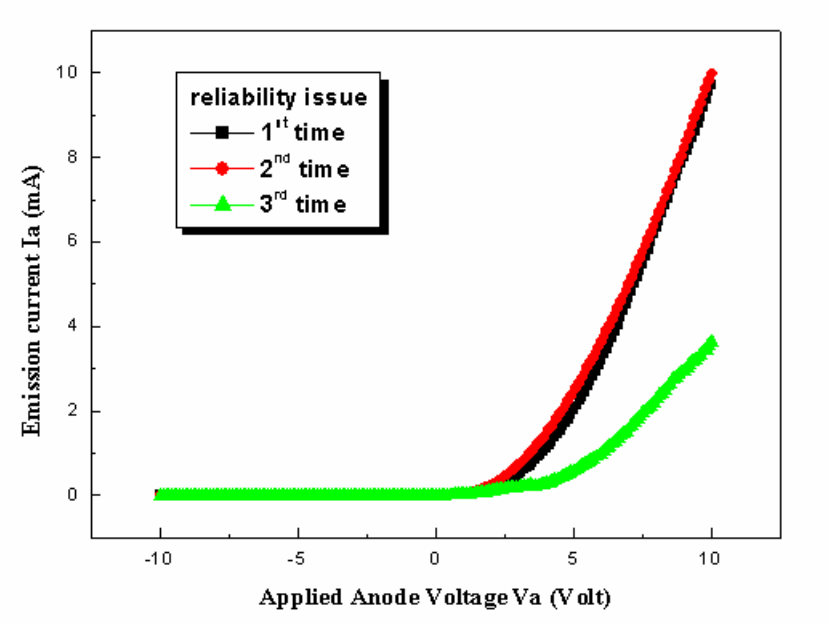


(b)

Figure 7-6 (a) Emission current (I_a) and anode voltage (V_a) characteristics of vertical CNT LFED with different heightS of CNTs, and (b) corresponding F-N plots.



(a)



(b)

Figure 7-7 Emission current reliability of vertical CNT LFED. The anode-to-emitter gap is 0.55 μm. (a) CNT growth time of 8 min. (b) CNT growth time of 20 min.

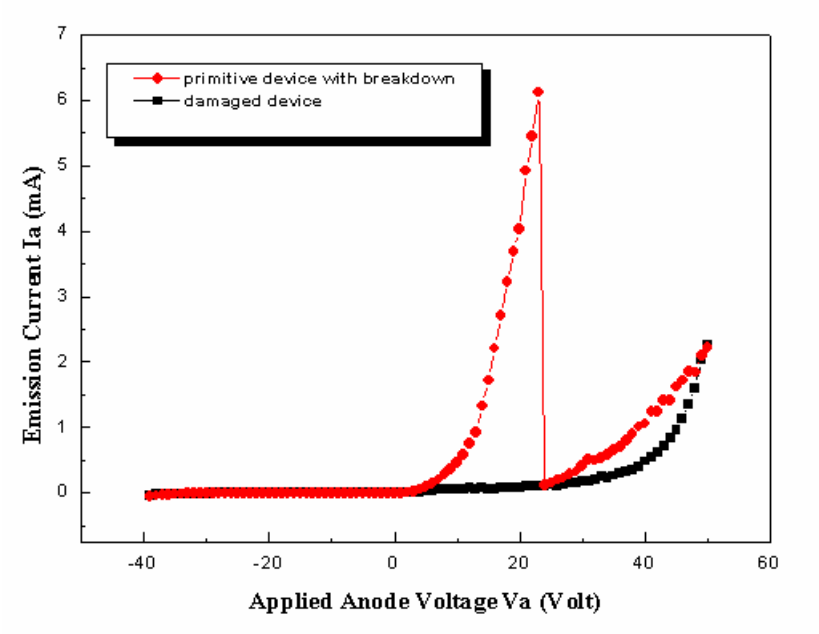
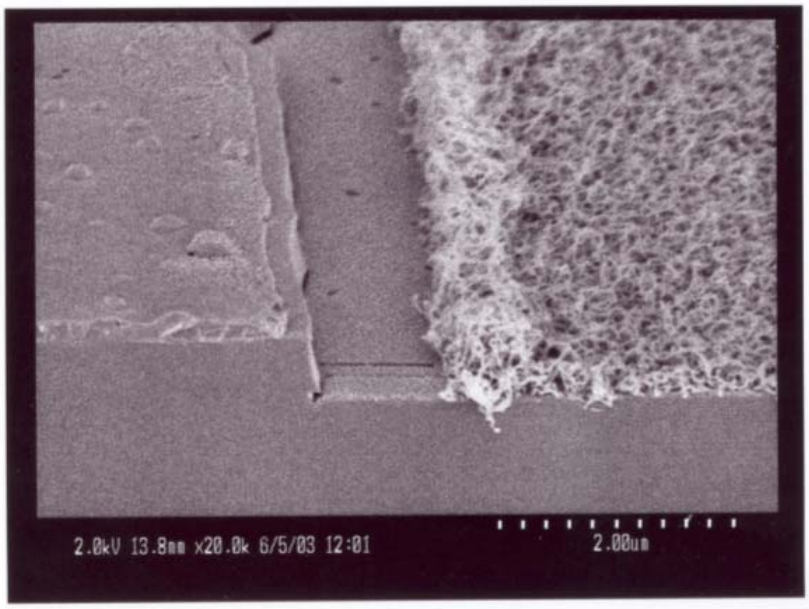
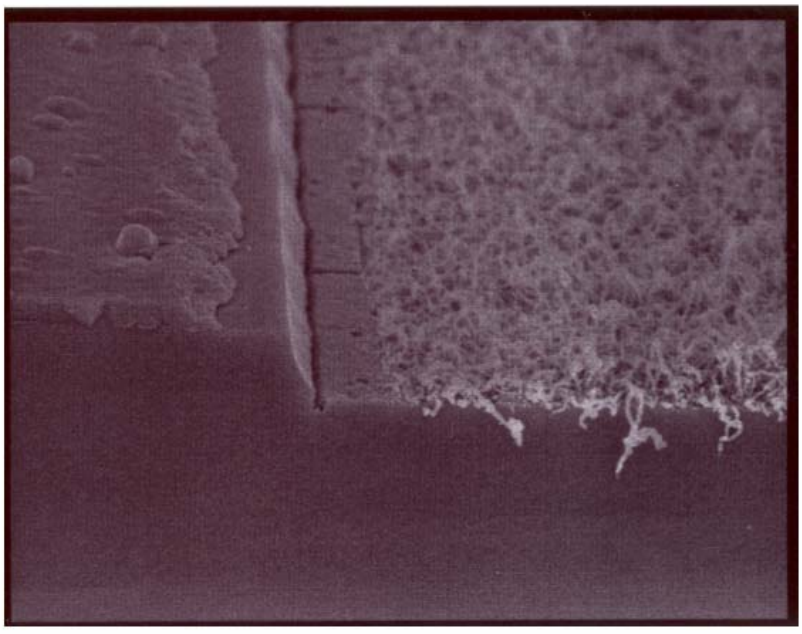


Figure 7-8 Field emission characteristics of burned-out of carbon nanotubes under strong electrical field



(a)



(b)

Figure 7-9 (a) SEM micrograph of vertical CNT LFED for original CNT morphology. (b) SEM micrograph of the CNTs LFED with burned-out or flew away CNTs.

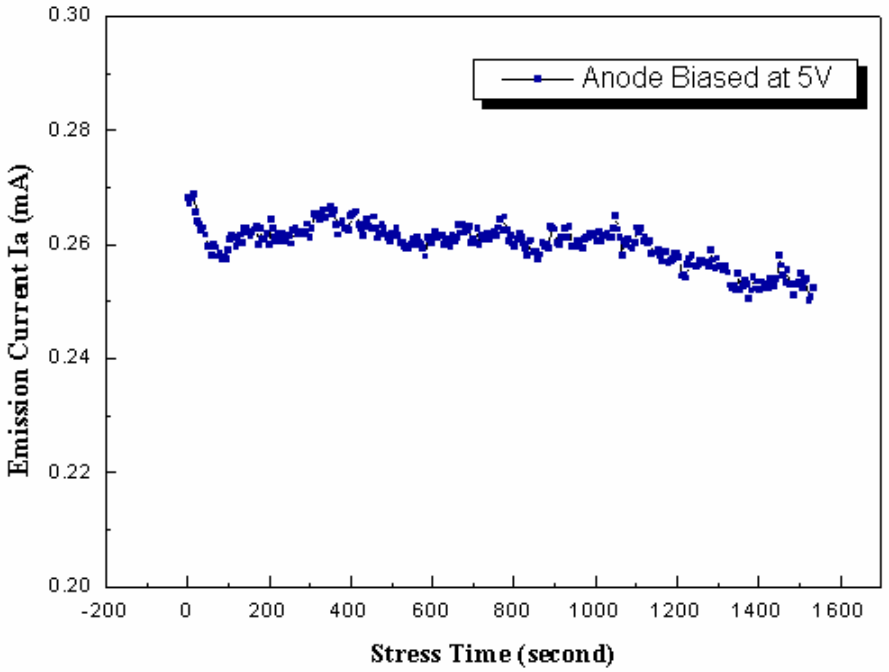


Figure 7-10 Emission current stability of the vertical CNT LFED over a period of 1500s.