Chapter 8

Summary and Conclusions

In this dissertation, carbon nanotubes synthesized by MPCVD and TCVD are used as field emitters for the nano-sized feature, which can provide large aspect ratio to increase the field enhancement factor β. However, density of carbon nanotubes synthesized by CVD is still very high and thus reduce the β value due to the field-screening effect. Therefore, the density distribution of carbon nanotubes is one of the critical parameters dominating the field emission characteristics of CNTs. To effectively enhance the field emission characteristics, some methods including partial oxidation of catalyst, oxide capping layer, morphology of CNTs with intermix of long and short nanotubes, pillar array of nanotubes and high density plasma post-treatment of nanotubes are used to improve the high density of CNTs and their field emission characteristics are also investigated.

First, an oxide capping layer deposited on a catalyst is used to control the density of CNTs. The results show that the field emission characteristics can be enhanced with a thin SiO layer on the catalyst layer as the precursor. Microwave plasma-enhanced chemical vapor deposition (MPCVD) and thermal chemical vapor deposition (TCVD) are used to grow nanotubes. For 3.5 nm Fe and 3.5 nm SiO on 3.5 nm Fe as a catalyst to grow nanotubes in MPCVD, the turn-on field can be decreased from 3.7 V/μm. to 2.2 V/μm and the field-emission current density increases from $3.8x10^{-6}mA/cm^2$ to $1.5x10^{-3}mA/cm^2$ when the applied field is 3.5 V/μm. For 5 nm Fe and 15 nm SiO on 5 nm Fe as a catalyst to grow nanotubes in TCVD, the turn-on electric field reduces from 3.8 V/μm to 1.8 V/μm and the emission current density increases from 7 x 10^{-8} mA/cm^2 to $1.77mA/cm^2$ at an applied electric field of 3.5 V/μm. In this method of oxide capping layer, the best field emission current density is not very high ($14.6mA/cm^2$ at 6 V/μm) although the turn-on field is as low as 2 V/μm. Besides, the threshold field is about 5.4 V/μm.

Partial oxidation of metal catalyst to control the density of CNTs is proposed to improve the field emission characteristics. By changing the oxidation temperature or oxidation time, it is possible to control the density of CNTs in the longer set. The results show that this method can produce two sets of CNTs with the structure of intermixture of long and short nanotubes and its field emission can also be enhanced. The turn-on filed can be reduced to 1.9V/μm and high field emission current density ($160mA/cm^2$) at an applied electric field of 6V/μm is achieved owing to effectively controlling of the density of CNTs. Besides, the threshold field is as low as about 3.9 V/μm.

A novel density control with the structure of intermixture of long and short carbon nanotubes are first synthesized by appropriately choosing the pre-treatment time and the contents of hydrogen during CNTs' growth. Due to the sparse nanotubes and relatively short distance between nanotube and anode, the group of longer CNTs will emit electrons earlier than the shorter set of CNTs. Therefore, the field screening effect is reduced and the turn-on field can be decreased. When the applied electric field increases to certain value, not only the longer set of CNTs emit electrons, but also the shorter set of CNTs will start to emit electrons. Finally, the field emission current density will increase very fast in a short range of electric field. When the pre-treatment times decrease from 10 to 5min, the turn-on fields decrease from 3.4 to 2.2V/μm and the field emission current density increases from 21 to 400mA/cm^2 at 6.46V/μm. The turn-on fields decrease from 4.4 V/μm to 2.2 V/μm and the field emission current density increases from 0.045mA/cm^2 to 400mA/cm^2 at 6.46V/μm when the contents of hydrogen increase from 10% to 50%. Besides, the best threshold field is about 3.64 V/μm with 5min pre-treatment of 50% hydrogen content. Therefore, we have successfully demonstrated that this novel density control of carbon nanotubes can greatly improve the field emission properties.

Pillar array of Cants with different R/H ratio (the ratio of distance between neighboring pillars (R) to the pillar height (H)) as field emitter by adjusting the growth condition is proposed to improve the field emission characteristics. The pillar is aligned perpendicular to the substrate surface and consists of CNTs with a number density of 10^9 cm^{-2}. When the R/H value is 1/3, ultra low turn-on field (~ 1 V/μm) and ultra low threshold field (2.9 V/μm) is obtained which is about 1/2-1/3 times lower than the values that have been reported. Besides, the ultra high field emission current density of 692mA/cm^2 at 7 V/μm is also the best value that has been reported. The field enhancement factor β of the FN equation was estimated to be approximately 25000 by setting the work function to be 5eV. The reason of very good field emission characteristic of pillar like CNTs arrays is probably due to that we envision the CNTs on the periphery of the pillar effect a dominant electric field concentration on their tops, acting as a major emission sites.

The effects of oxygen plasma post-treatment (PPT) on the morphology and field emission properties of carbon nanotube (CNT) arrays grown on silicon substrates are proposed. Modifying the surface morphology of CNTs has been achieved by oxygen plasma post-treatments. SEM images revealed reduced densities of CNTs after O_2 plasma post-treatment. Raman spectra show an increase in the number of defects which served as field-emission sites when the plasma power or treatment time with plasma increased. Transmission electron microscopy (TEM) images are used to identify the quality of nanotubes so that we can clearly find evidences of improvement in the field emission properties after plasma treatment. The field emission characteristics confirm the improvement of field emission properties under proper PPT conditions. The turn-on electric field decreases from 4.8 to 2.5 V/μm for untreated and PPT conditions of a plasma power of 250 W and an etching time of 90 s, respectively, and the field emission current density increase from 78.7 μA/cm^2 to 18 mA/cm^2 at an electric field of 5.5 V/μm. Besides, the best threshold field is about 4.92 V/μm with 250W and 90s plasma post-treatment case. The experimental results reveal that improved emission properties can be achieved by optimizing the density of CNTs and the defects on nanotubes produced by plasma under proper plasma treatment conditions.

Low turn field, high field emission current density and low threshold field are required for field emission display application. In our proposed methods, pillar arrays of CNTs as field emitters are probably the best candidate for diode type field emission display because of its ultra low turn-on field (~ 1 V/μm), ultra low threshold field (2.9 V/μm) and ultra high field emission current density (692mA/cm^2 at 7 V/μm).

As for vacuum micro-electronics' application, a vertical lateral field emission device (LFED) of CNTs is fabricated. 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 low emission current fluctuation (~ ± 3.5% for 1500s) confirms that the field emission current of this lateral field emission diode is very stable.