Chapter 1 Introduction

1.1 Overview of Vacuum Microelectronics and its Applications1.1.1 History of vacuum microelectronics

Since the first transistor was invented by Bardeen, Brattain, and Shockley in 1948[1.1], vacuum tubes have been gradually replaced by solid state electronic devices due to the tiny volume, low cost , better reliability and more power efficiency of solid state devices. With great improvements on semiconductor manufacturing technology for the past decades, the so called vacuum microelectronic devices using the professional micro fabrication technology have been successfully fabricated and gave a new life to vacuum electronics. The vacuum microelectronic devices have many superior advantages as compared with solid state devices. The superiorities of the vacuum microelectronic devices are:

(a) No saturation of drift velocity in the vacuum microelectronic devices. The saturation drift velocity is limited to less than 3×10^7 cm/s in all semiconductor due to scattering mechanism whereas the saturation drift velocity in vacuum is limited theoretically to 3×10^{10} cm/s and practically to about $6-9 \times 10^8$ cm/s [1.2].

(b) No temporary or permanent radiation effect. Since the electrons fly in the

vacuum, there is negligible radiation effect in vacuum devices due to no medium being damaged [1.3].

(c) Almost temperature insensitivity. Since there is no medium for electrons fly in the vacuum, there is no lattice scattering or bulk carrier generation/recombination. Therefore, the vacuum microelectronic devices can suffer to 500°C or above as long as the structures of the vacuum devices do not destroyed [1.3].

 Table 1-1 shows the comparison between vacuum microelectronic and

 semiconductor devices.

A brief history of the development and theory is necessary for better understanding vacuum microelectronics. In 1928, R. H. Fowler and L. W. Nordheim published the first theory of electron field emission (Fowler- Nordheim theory) from metals using quantum mechanics [1.4]. This theory is different from thermionic emission, which metal has to be heated so that some of the electrons in the metal gain enough thermal energy to overcome the metal/vacuum barrier. According to the Fowler-Nordheim theory, an applied electric field of approximately 10⁷ V/cm is needed for electrons to tunnel through the sufficiently narrow barrier. To reach this high field at reasonable applied voltage, producing the field emitters into protruding objects is essential to take advantage of field enhancement. It was not until 1968 when C. A. Spindt camp up with a fabrication method to create very small dimension metal cones that vacuum microelectronic triodes became possible [1.5]. From the late 1960s to the year 1990, Ivor Brodie, Henry F. Gray, and C. A. Spindt made many contributions to this field. Also, most of research was focused on the devices similar to the Spindt cathode during the past three decades.

In 1991, a group of research of the French company LETI CHEN reported a microtip display at the fourth International Vacuum Microelectronics Conference [1.6]. Their display was the first announcement of a practical vacuum microelectronic device. From then on, a great amount of researchers all over the world devoted themselves to this interesting, challenging, and inventive field. Part of the work focused on fabricating very small radius silicon tip by utilizing modern VLSI technology [1.7-1.8]. Some of them increased the emission current by coating different metals, such as W, Mo, Ta, Pt etc., even diamond on field emission arrays [1.9-1.11]. Different device schemes also have been proposed to enhance the emission current density, stability, and reliability.

1.1.2 Theory Background

Electron field emission is a quantum mechanical tunneling phenomenon of electrons extracted from the conductive solid surface, such as a metal or a semiconductor, where the surface electric field is extremely high. If a sufficient electric field is applied on the emitter surface, electrons will be emitting through the surface potential barrier into vacuum, even under a very low temperature. In contrast, thermionic emission is the hot electron emission under high temperature and low electric field. Fig. 1-1(a) demonstrates the band diagram of a metal-vacuum system.

Here W_0 is the energy difference between an electron at rest outside the metal and an electron at rest inside the metal, whereas W_f is the energy difference between the Fermi level and the bottom of the conduction band. The work function ϕ is defined as $\phi = W_0 - W_f$. If an external bias is applied, vacuum energy level is reduced and the potential barrier at the surface becomes thinner as shown in Fig. 1-1(b). Then, an electron having energy "W" has a finite probability of tunneling through the surface barrier. Fowler and Nordheim derive the famous F-N equation (1.1) as follow [1.4]:

$$J = \frac{AE^{2}}{\phi t^{2}(y)} \exp[-B\phi^{\frac{3}{2}}v(y)/E], \qquad (1-1)$$

where J is the current density (A/cm²). E is the applied electric field (V/cm), ϕ is the work function (in eV), A = 1.56×10^{-6} , B = -6.831×10^{-7} , y = $3.79 \times 10^{-4} \times 10^{-4} E^{1/2}/\phi$, $t^2(y) \sim 1.1$ and v(y) can be approximated as [1.12]

$$v(y) = \cos(0.5\pi y),$$
 (1-2)

or

 $v(y)=0.95-y^2.$

(1-3)

Typically, the field emission current I is measured as a function of the applied voltage V. Substituting relationships of $J = I/\alpha$ and $E = \beta V$ into Eq.(1-1), where α is the emitting area and β is the local field enhancement factor of the emitting surface, the following equation can be obtained

$$I = \frac{A\alpha\beta^2 V^2}{\phi t^2(y)} \exp[-Bv(y)\frac{\phi^{\frac{3}{2}}}{\beta V}].$$
(1-4)

Then taking the log. form of Eq. (1-4) and $v(y) \sim 1$

$$\log(\frac{I}{V^2}) = \log[1.54 \times 10^{-6} \frac{\alpha \beta^2}{\phi t^2(y)}] - 2.97 \times 10^7 (\frac{\phi^{\frac{3}{2}} v(y)}{\beta V}), \qquad (1-5)$$

from Eq. (1-5), the slope of a Fowler-Nordheim (F-N) plot is given by

$$S \equiv slope_{FN} = -2.97 \times 10^7 \left(\frac{\phi^{\frac{3}{2}}}{\beta}\right),$$
 (1-6)

The parameter $\boldsymbol{\beta}$ can be evaluated from the slope S of the measured F-N plot if the

work function ϕ was known

$$\beta = -2.97 \times 10^7 (\frac{\phi^2}{S}) \quad (\text{cm}^{-1}), \qquad (1-7)$$

The emission area α can be subsequently extracted from a rearrangement of Eq. (1-5)

$$\alpha = (\frac{I}{V^2}) \frac{\phi}{1.4 \times 10^{-6} \beta^2} \exp(\frac{-9.89}{\sqrt{\phi}}) \exp(\frac{6.53 \times 10^7 \phi^{\frac{3}{2}}}{\beta V}) \quad (\text{cm}^2).$$
(1-8)

For example, the electric field at the surface of a spherical emitter of radius r concentric with a spherical anode (or gate) of radius r+d can be represented analytically by

$$E = \frac{V}{r} \left(\frac{r+d}{d}\right),\tag{1-9}$$

Though a realistic electric field in the emitter tip is more complicated than above equation, we can multiply Eq.(1-9) by a geometric factor β to approximate the real condition.

$$E_{tip} \equiv \text{function of } (\mathbf{r}, \mathbf{d}) = \beta^{\mathsf{T}} \frac{V}{r} \left(\frac{r+d}{d}\right), \qquad (1-10)$$

where r is the tip radius of emitter tip, d is the emitter-anode(gate) distance and β is a geometric correction factor [1.13].

For a very sharp conical tip emitter, where d >> r, E_{tip} approaches to $\beta^{(V/r)}$. And for r>>d, E_{tip} approaches to $\beta^{(V/d)}$ which is the solution for a parallel-plate capacitor and for a diode operation in a small anode-to-cathode spacing. As the gated FEA with very sharp tip radius, Eq. (1-10) can be approximated as:

$$E_{tip} = \beta^{(V/r)}.$$
(1-11)

Combining E= β V and Eq. (1-11), we can obtain the relationship:

$$E_{tip} = \beta V = \beta^{(V/r)}, \text{ and } \beta^{=} \beta r.$$
 (1-12)

The tip radius r is usually in the range from a few nm to 50 nm, corresponding to the parameter β ranging from 10^{-1} to $10^{-2.96}$

Besides, transconductance g_m of a field emission device is defined as the change in anode current due to a change in gate voltage [1.4].

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$$g_m = \frac{\partial I_C}{\partial V_g} |_{\rm Vc} , \qquad (1-13)$$

Transconductance of a FED is a figure of merit that gives as an indication of the amount of current charge that can be accomplished by a given change in grid voltage. The transconductance can be increased by using multiple tips or decreasing the cathode-to gate spacing for a given cathode-to-anode spacing.

According to the equations above mentioned (especially Eq.1-5), the following approaches may therefore be taken to reduce the operating voltage of the field emission devices:

- (1) Find techniques to reproducibly sharpen the tips to the atomic level (increase β).
- (2) Lower the work function of the tip (ϕ)
- (3) Narrow the cone angle (increase β).
- (4) Reduce the gate-opening diameter (increase β).

1.1.3 Applications of Vacuum Microelectronics

Due to the superior properties of vacuum microelectronic devices, potential applications include high brightness flat-panel display [1.14-1.18], high efficiency microwave amplifier and generator [1.19-1.21], ultra-fast computer, intense electron/ion sources [1.22-1.23], scanning electron microscopy, electron beam lithography, micro-sensor [1.24-1.25], temperature insensitive electronics, and radiation hardness analog and digital circuits.

Solid-state devices, such as Si bipolar transistor, impact avalanche transit time (IMPATT) diodes, and GaAs FETs [1.26], are typically used in the low power (up to 10 W) and frequency up to 10 GHz range. Vacuum devices are also available for high power and high frequency application. Traditional multi-terminal vacuum tubes, like triodes, pentodes, and beam power tubes, and distributed-interaction devices, such as traveling wave tubes (TWTs), backward-wave oscillators (BWOs) are those typical vacuum devices. The performance of FEAs in conventionally modulated power tubes, like TWT, is determined primarily by their emission current and current density

capability. On the other hand, the application of FEAs in the microwave tubes in which modulation of the beam is accomplished via modulation of the emission current at source, such as capacitance and transconductance. Successful operation of a gated FEA in a 10 GHz TWT amplifier with conventional modulation of electron beam has been demonstrated by NEC Corporation of Japan [1.27]. The amplifier employed a modified Spindt-type Mo cathode with circular emission area of 840 µm in diameter. The modified cathode structure incorporated a resistive poly-Si layer as a current limiting element. The emission current from the cathode was 58.6 mA. The prototype TWT could operate at 10.5 GHz with the output power of 27.5 W and the gain of 19.5 dB. The bandwidth of the tube was greater than 3 GHz. The prototype was operated for 250 h.

Among these wide range applications of vacuum microelectronics devices, the first commercial product could be the field emission flat-panel display. The field emission fluorescent display is basically a thin cathode ray tube (CRT), which was first proposed by SRI International and later demonstrated by LETI [1.6].

Lower power consumption, light weight and small volume are the necessary characteristics for flat-panel displays. LCDs are the most popular flat-panel displays and are wildly used in many portable computers, consumer electronics. However, LCDs have some drawbacks such as poor viewing angle, temperature sensitivity, high power consumption and low brightness. Thus, some opportunities are waiting for the other display such as FEDs.

FED features all the pros of the CRTs in image quality and is flat and small volume. The schematic comparisons are revealed in Fig.1-2. The operation of CRTs involves deflection of the beam in such a way that the electron spot scans the screen line-by-line. In FEDs, multiple electron beams are generated from the field emission cathode and no scanning of beams is required. The cathode is a part of the panel substrate consists of an X-Y electrically addressable matrix of field emission arrays (FEAs). Each FEA is located at the intersection of a row and a column conductor, with the row conductor serving as the gate electrode and the column conductor as the emitter base. The locations where the rows and columns intersect define a pixel. The 40000 pixel area and number of tips are determined by the desired resolution and luminance of the display. Typically, each pixel contains an FEA of 4-5000 tips. The emission current required for a pixel varies from 0.1 to 10 µA, depending on the factors such as the luminance of the display, phosphor efficiency and the anode voltage.

Compared to the active matrix LCDs, FEDs generate three times the brightness with wilder viewing angle at the same power level. Full color FEDs have been developed by various research groups from different aspects such as PixTech, Futaba, Fujitsu, Samsung, are presently engaged in commercially exploiting FED.

1.2 Cold Cathode Structure and Materials for Field Emission Displays

1.2.1 Spindt-type Field Emitter

The "Spindt" cathode was first proposed by C. A. Spindt in 1968[1.28]. It had been widely studied and various cathode materials/structures had been developed since the proposal of "Spindt" cathode. Figure 1-3 demonstrated the scanning electron microscope (SEM) and schematic images of a Spindt type field emission triode [1.29], which was invented by Spindt of SRI and improved for the electron source of high-speed switching devices or microwave devices [1.30]. Meyer of LETI presented the capability of using Spindt-type emitters for a display in 1970s [1.31] and stabilized the field emission from Spindt-type emitters by introducing a resistive layer as the feedback resistance. This proposal triggered the development of field emitters 411111 as an electron source of displays by researchers and electronics makers in 1990. Some research groups have successfully fabricated commercial FED products based on Spindt type field emitters such as Futaba, Sony/Candesent, Futaba and Pixtech.[1.32], the products above mentioned companies are shown in Figures 1-4.

The merits of the Spindt type field emitters are summarized as following: (1) High emission current efficiency, more than 98% anode current to cathode current can be achieved for the symmetric structure of Spindt tip and the gate hole, the lateral electric field to the metal tip can be cancelled out. (2) The fabrication is self-aligned, easy process; uniform field emission arrays can be fabricated easily. However, there are some existing drawbacks of Spindt type field emitters when fabricating Spindt type FED such as (1) High gate driving voltage required; for a Spindt type field emission triode with 4 μm gate aperture, the driving voltage is typically more than 60 V, which results in the high cost of the driving circuits. To reduce the gate driving voltage, frontier lithography technologies such as E beam lithography must be applied to reduce the gate aperture to the sub-micron level. (2) The emission property degrades for the chemically instable of the metal tips. (3) Huge, expensive high vacuum deposition system required during fabricating large area Spindt type FED.

1.2.2 Si tip field emitters

An alternative approach to fabricate tip type field emitters is to fabricate the Si tip field emitters based on the semiconductor fabricating process. Figures 1-5(a)-(c) depict the SEM micrographs of Si tips array, Si tip field emission triodes array formed by chemical mechanical polishing (CMP) and double gate of Si field emitter arrays[1.33-1.34]. Symmetric device structure and similar advantages with Spindt type field emitters can be obtained. However, high temperature oxidation sharpening process prohibits Si tip from large area fabrication.

1.2.3 Low-Work-Function or Negative-Electron-Affinity Cold Cathodes

The cold cathodes with low work function or negative electron affinity are with

wide band gap materials. Their electron energy level of conduction band is higher than the vacuum level [1-35]. Therefore, it is easy for electrons to escape into the vacuum once electrons are pumping to the conduction band. However, it is really a big problem because more external energy is needed to pump electrons into the conduction band in those wide band-gap materials.

It is reported by Kumar et al.[1.36] that the amorphous diamond-like(DLC) films has a low work function (~0.2-0.7eV) and reached 10 A/cm² field emission current density at $20V/\mu$ m electric field. Therefore, coating DLC or diamond film onto the Spindt or other tips has been widely studied to lower the turn-on voltage.

Some of these cold cathodes had been used in high-speed switch or high vacuum pressure gauge sensor. But neither one successfully achieved practical application in field emission display. The Spindt type field emitters are the only one that has been used in the application of field emission display. However, they are not acceptable for display market due to some existing drawbacks mentioned above.

1.2.4 Carbon-Nanotube(CNT) Field Emitter

Since the discovery of CNTs in 1991, they have been attracting much attention for their unique physical and chemical properties, such as their high aspect ratio, high mechanical strength, chemical stability, super-thermal conductivity, and electron emission properties [1.37-1.38]. Therefore, one of the most potential applications of carbon nanotubes is as the field emission material in vacuum microelectronics, such as flat- panel field-emission displays (FEDs), nanoprobes of atomic force microscopes (AFMs), microsensors, or scanning tunneling microscopes (STMs) and microsized intense electron sources[1.14,1.22-1.24,1.28].

According to Fowler-Nodheim theory, the electric field at the apex of a needle-shaped tip is enhanced by a factor $\beta = h/r$, where h is the height of the tip and r is the radius of curvature of the tip apex. The carbon nanotube is a stable form of carbon and can be synthesized by several techniques. They are typically made as threads about 10-100 nm in diameter with a high aspect ratio (>1000). These geometric properties, coupled with their high mechanical strength and chemical stability, make carbon nanotubes attractive as electron field emitters. Several groups have recently reported good electron field emission from nanotubes [1.39-1.41].

In 1999, Samsung pronounced a 4.5-inch carbon nanotube based field emission display. They mixed a conglomeration of single-walled CNTs into a paste with a nitrocellulose binder and squeezed the concoction through a 20-µm mesh onto a series of metal strips mounted on a glass plate. As the CNTs emerged from the mesh, they were forced into a vertical position. The metal strips with the CNTs sticking out of them served as the back of the display. The front of the display was a glass plate containing red, green, and blue phosphors and strips of a transparent indium-tin-oxide

anode running from side to side. The glass plates were separated by spacers with the thickness of 200 μ m. Once assembled, the edges were sealed and air was pumped out of the display.

Samsung's field emission display (Fig. 1-6) could be the precursor of a new generation of more energy efficient, high performance flat panel displays for portable computers [1.42]. The CNTs appear to be durable enough to provide the 10000hr lifetime considered being a minimum for an electronic product. The panel consumes just half the power of an LCD to generate an equivalent level of screen brightness. They could also be cheaper than LCDs or other types of field emission displays being developed. Until now, at last five major Japanese electronic manufactures are working on this technology.

1.2.5 Surface Conduction Electron Emitter (SCE)

The SED, based on a new type of flat-panel display technology, was created Canon and Toshiba. Like conventional CRTs, SEDs utilize the collision of electrons with a phosphor-coated screen to emit light. The key technology to the electron emitters begins with the creation of an extremely narrow slits (~ several nanometers) between two electric poles in thin film of PdO (Palladium Oxide). Electrons are emitted from one side of the slit when approximately 10V of electricity are applied. Some of these electrons are scattered at the other side of the slit and accelerated by the voltage (approximately 10 kV) applied between the glass substrates; causing light to be emitted when they collide with the phosphor-coated glass plate. The PdO film is coated by inject printing or screen- printing technology and this is a low cost process. The major problem of SED is that the efficiency is still low and the power consumption will be very high. Figure 1-7 shows the fabrication of nano-gap, structure and a 36-inch display of SED [1.43-1.44].

1.3 Motivation

It is important to find a cold cathode with low operating voltage, high emission current, sufficient stability and well reliability when considering its commercialization to field emission display. According to the F-N theory, to obtain the high field emission current at low operating voltage, cold cathode material with low work function is indispensable and the field enhancement factor β and emission area α should be as large as possible.

To obtain a large β , the conventional method is to fabricate sharp tips, which needed special techniques or complicated fabrication process, such as large oblique-angle thermal evaporation or sputtering to fabricate sharp metal cones, high temperature oxidation to sharpen silicon tips, or anisotropic etching of silicon using KOH to produce sharp tip molds. Recently, carbon nanotubes (CNTs) have drawn much attention due to its unique physical and chemical properties. Because of its nanometer-size feature and ease to fabricate, CNTs have been regarded as a strong candidate for field-emission displays. The density of CNTs plays a crucial role in their field emission properties. For film with high CNT density, the screening effect reduces the field enhancement and thus reduces the emitted current [1.45-1.47]. Therefore, it is important to control the density of CNTs in field emission applications. However, the density of carbon nanotubes grown by chemical vapor deposition such as microwave plasma enhanced chemical vapor deposition (MPCVD) or thermal chemical vapor deposition (TCVD) still can't be controlled effectively.

In this thesis, carbon nanotubes synthesized by MPCVD and TCVD were used as field emitters for the nano-sized feature, which can provide large aspect ratio to increase the field enhancement factor β . The high density of CNTs can also provide large field emission sites (the emission area α also be increased). The field emission characteristics of the CNTs with different morphology suggested that the field enhancement factor β is strongly affected by the density of CNTs. For high-density CNTs, the field-screening effect reduces the β value and the emission current. Well control of density and surface morphology of CNTs is thus required for future applications. To effectively control the densities of nanotubes, 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 were used to improve the high density of CNTs and their field emission characteristics were also investigated.

Besides, a vertical lateral field emission device (LFED) based on carbon nanotubes (CNTs) were fabricated and characterized. It combines high-performance nanomaterials with mature solid-state fabrication technology to produce miniaturized vacuum devices with superior field emission characteristics.

1.5 Thesis Organization



4111111 the density of carbon nanotubes (CNTs). In this thesis, we have completely proposed some useful methods including partial oxidation of metal catalyst, oxide capping layer on metal catalyst, control of pre-treatment condition during nanotubes' growth and plasma post-treatment to improve the field emission characteristics of CNTs for field emission display. We have also fabricated a vertical lateral field emission device of CNTs.

Chapter 1 overviewed the vacuum microelectronics, the basic field emission theory, some cold cathode materials for field emission display and motivation of this thesis.

Effects of oxide capping layer of CNTs grown by MPCVD and TCVD were demonstrated in chapter 2. Oxide layers with different thickness capping on catalyst metal were used to control the density and morphology of CNTs and achieved to improve the field emission characteristics.

Chapter 3 demonstrated that partial oxidation of metal catalyst before CNTs' growth could be used to control the density of CNTs and achieved field emission improvement.

A novel structure with intermixture of long and short CNTs by controlling the flow rate of H_2 and pre-treatment time during CNTs' growth was described in chapter 4. This method not only reduced the density of CNTs but also kept the field emission sites not to be reduced.

Chapter 5 showed that field emission enhancement could achieve by adjusting the ratio of distance between the neighboring pillars to the pillar height. A post-treatment of CNTs by high-density oxygen plasma to improve the field emission characteristics was revealed in chapter 6.

The low turn-on voltage of lateral field emission device of carbon nanotubes fabricated by controlling the distance between inter-electrodes was demonstrated in chapter 7. Finally, the conclusions and recommendations for future researches were provided in chapter 8 and 9, respectively.



Table 1-1 Comparison between vacuum microelectronics and solid-state electronics.

-	Solid State	Vacuum
ltems	Microelectronics	Microelectronics
Current Density	$10^4 - 10^5 ~(\text{A/cm}^2)$	similar
Turn-on Voltage	$0.1 - 0.7 \; V$	5 – 300 V
Structure	solid/solid interface	solid/vacuum interface
Electron Transport	in solid	in vacuum
Electron Velocity	3×10 ⁷ (cm/sec)	3×10 ¹⁰ (cm/sec)
Flicker Noise	due to interface	due to emission
Thermal & Short Noise	comparable	comparable
Electron Energy	< 0.3 eV	a few to 1000 eV
Cut-off Frequency	< 20 GHz (Si) &	< 100 – 1000 GHz
	100 GHz (GaAs)	
Power	small – medium	medium – lar ge
Radiation Hardness	poor	excellent
Temperature Effect	-30 – 50 ℃	< 500 ° C
Fabrication & Materials	well established (Si) & fairly well (GaAs)	not well established



Fig. 1-1 Energy diagrams of vacuum-metal boundary: (a)without external electric

field; and (b) with an external electric field





(b)

Fig. 1-2 The schematic diagram of (a) conventional cathode ray tube (CRT), (b) field emission display (FED)





Fig. 1-3 The SEM micrograph of (a) Spindt type triodes array, (b) Spindt type field emission triode, and the schematic image of (c) Spindt type triode array



Motorola 5.6" color FED



Pixtech 15" color FED

(b)



Fig. 1-4 The FED products based on Spindt type field emitters, (a) motorola 5.6" color FED, (b) Pixtech 15" color FED, (c) Futaba 7" color FED and (d) Sony/Candescent 13.1" color FED





Fig. 1-5 (a) Si tip formed by isotropic etching and (b) Si tip field emission triodes array formed by CMP (c) cross section view of double gate Si field emitter

arrays





Fig. 1-6 (a) SEM image of CNT cathode from Samsung's FED, (b) a 4.5-inch FED from Samsung, the emitting image of fully sealed SWNT-FED at color mode with red, green, and blue phosphor columns, and (c) a prototype of 5" CNT flat panel display by Samsung







(c)

Figure 1-7 (a) Fabrication of tunneling nano-gap (b) structure of SED (c) a 36-inch prototype of surface conduction electron emitter display