Development of carbon nanotubes for vacuum electronics application

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**DEVELOPMENT OF CARBON NANOTUBES FOR
VACUUM ELECTRONICS APPLICATION**

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SCHOOL OF ELECTRICAL AND ELECTRONICS ENGINEERING

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**Development of Carbon Nanotubes for
Vacuum Electronics Application**

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Abstract

Traveling-wave Tube Amplifier (TWTA) has been widely used in satellite applications due to its high bandwidth, capabilities in high frequency operation, and high thermal tolerance. In the miniaturization of TWTA, Planar Helix-Slow Wave Structure (PH-SWS) has been proposed, which can be fabricated using Silicon-based microfabrication techniques. To utilize this PH-SWS in TWTA, a miniaturized, high current density field emitter is needed for its operation in TWTA. Carbon Nanotubes (CNTs) has been proposed as a promising field emitting material. In this study, the main objective is to design fabricate a small size, high current density field emitter which is capable of delivering signal gain of ~20 dB in PH-SWS TWTA.

First, simulation study is carried out on the effect of electron beam current to the signal amplification performance of PH-SWS TWTA. The simulation is carried out using CST STUDIO SUITE. From the simulation, it is found that the signal gain of TWTA increases when the electron beam current increases from 2 to 25 mA. To achieve signal gain above 20 dB, electron beam current of > 6 mA, or current density of > 0.8 A/cm² rectangular emitting area is needed. from 1250x600 μm (0.75 mm²) rectangular emitting area is needed.

After obtaining the required FE current density, it is important to select the most suitable technique to synthesize high FE current density CNTs. CNTs are grown using two approaches: plasma enhanced chemical vapor deposition (PECVD) and thermal chemical vapor deposition (TCVD). For TCVD technique, two types of catalyst sources are attempted, pre-deposited catalyst and floating catalyst sources. Among the investigated growth technique, it is found that floating catalyst TCVD technique yields higher FE current density due to the high field enhancement on CNT tips.

To reduce the inter-tube screening effect, CNTs can be grown in separated islands by means of photolithography technique. However, CNTs growth using floating catalyst CVD technique is non-selective, which is challenging to grow CNTs in separated islands using such CVD technique. To grow CNTs in separated islands, CNTs are grown on Si and SiO₂ surfaces at growth temperatures from 760 to 880 °C. Selective growth of CNTs on Si is achieved at growth temperature of 790 °C.

By using the obtained selective growth condition, array of CNT bundles is grown on Si/SiO₂ structure, obtaining FE current density of ~ 90 mA/cm². However, it is found that CNTs possess random alignment at the obtained selective growth condition of 790 °C, reducing the field enhancement on CNT bundles. To improve the FE current density, CNT bundles are confined in pre-fabricated SiO₂ pits to retain its geometrical shape. From the FE measurement, CNT bundles confined in 2 µm and 0.5 µm diameters pits achieve FE current density of > 333.33 mA/cm² and > 1 A/cm², respectively. The obtained current density of > 1 A/cm² can be expected to achieve the research objective of > 20 dB signal gain in PH-SWS TWTA, as simulated earlier.

To explore further improvement in FE current density, the FE properties of screen-printed CNTs paste with ~5 nm diameter single-walled CNTs is explored. High FE current density of 9 A/cm² is obtained consistently from 0.5×1 mm screen-printed cathode. By using the obtained FE condition, hexagonal mesh is designed and simulated to obtain the optimized mesh design. From the simulation, 20 mA current can be expected to emit from the optimized hexagonal mesh, which corresponds to ~28 dB signal gain in PH-SWS TWTA.

Table of Content

Acknowledgements.....	iii
Abstract.....	v
Table of Content	vii
List of Figures	xii
List of Tables	xix
List of Abbreviations	xxi
Chapter 1: Introduction and Overview	1
Chapter 2: Literature Review.....	5
2.1 Basic Operations and Development Trends in Satellite Communication.....	5
2.1.1 Overview and Progressing Trend.....	5
2.1.2 Satellite Communication System and Operation Bands	8
2.2 Signal Amplifiers in Satellite Communication	10
2.2.1 Historical Development in Signal Amplifiers.....	11
2.2.2 Comparison between SSPA and MVED.....	13
2.2.3 SSPA and MVED in Satellite Application	17
2.2.4 Traveling Wave Tube Amplifiers (TWTAs)	20
2.2.4a Operation Theory of Traveling Wave Tube Amplifiers (TWTAs).....	21
2.2.4b Development and Challenges of Traveling Wave Tube Amplifiers (TWTAs)	24
2.3 Types of Electron Emitters for Traveling Wave Tube Amplifier (TWTA).....	26

Table of Content

2.3.1 Thermionic Emission	27
2.3.2 Field Emission (FE)	28
2.4 Development of Field Emission (FE) Cathode	32
2.4.1 Spindt-type Cathode.....	33
2.4.2 Nanostructured Cathode.....	36
2.5 Carbon Nanotubes (CNTs) as Field Emitter	39
2.5.1 Introduction to Carbon Nanotubes (CNTs).....	39
2.5.2 Simulated Field Emission (FE) Characteristics of Carbon Nanotubes (CNTs).....	42
2.5.3 State-of-the-art High Field Emission (FE) Carbon Nanotubes (CNTs).....	45
Chapter 3: Motivation and Objectives	50
3.1 Motivation	50
3.2 Objectives.....	52
Chapter 4: Simulation of Planar Helix-Slow Wave Structure Traveling Wave Tube Amplifier	54
4.1 Introduction	54
4.2 Effect of Electron Beam Current on the Signal Gain of PH-SWS TWTA	55
4.3 Design and Simulation of Beam-Forming Electrode for PH-SWS TWTA	62
4.4 Summary	64
4.5 Publications	65
Chapter 5: Field Emission (FE) Properties of Carbon Nanotubes: Plasma-Enhanced Chemical Vapour Deposition (PECVD) Growth Technique	66
5.1 As-Grown and Densified PECVD-grown Carbon Nanotube (CNT) films.....	66

Table of Content

5.1.1 Experimental Method.....	66
5.1.2 Results and Discussion	67
5.2 Three-Dimensional Carbon Nanotube (3D CNT) Network.....	72
5.2.1 Experimental Method.....	72
5.2.2 Results and Discussion	74
5.3 Summary	81
5.4 Publications	82
Chapter 6: Field Emission (FE) Properties of Carbon Nanotubes (CNTs): Thermal Chemical Vapour Deposition (TCVD) Growth Technique	83
6.1 Pre-Deposited Catalyst TCVD-grown Carbon Nanotube (CNT) films	83
6.1.1 Experimental Method.....	84
6.1.2 Results and Discussion.....	84
6.2 Floating Catalyst TCVD-grown Carbon Nanotube (CNT) films.....	90
6.2.1 Experimental Method.....	91
6.2.2 Results and Discussion	91
6.3 Summary	98
6.4 Publications	98
Chapter 7: Selective Growth of Carbon Nanotubes (CNTs) on Si/SiO ₂ Structure using Floating Catalyst Chemical Vapour Deposition Technique	100
7.1 Introduction	100
7.2 Experimental Method.....	102
7.3 Results and Discussion.....	103

Table of Content

7.4 Summary	113
7.5 Publication.....	114
Chapter 8: Fabrication of Carbon Nanotubes (CNTs) Field Emitter Array.....	115
8.1 Introduction	115
8.2 Experimental Method.....	116
8.3 Results and Discussion.....	119
8.4 Summary	130
8.5 Publication.....	131
Chapter 9: Field Emission (FE) Properties of Screen-Printed Carbon Nanotubes (CNTs) Field Emitter.....	132
9.1 Introduction	132
9.2 Experimental Method.....	133
9.3 Results and Discussion.....	135
9.4 Summary	139
9.5 Publication.....	140
Chapter 10: Design and Simulation of Hexagonal Mesh Screen-Printed CNT Field Emitter	141
10.1 Introduction	141
10.2 Design and Simulation of Hexagonal Mesh.....	143
10.3 Integration of Screen-Printed Carbon Nanotubes (CNTs) Field Emitter in Planar Helix-Slow Wave Structure Traveling Wave Tube Amplifier (PH-SWS TWTA).....	154
10.4 Summary	157

Table of Content

10.5 Publication.....	157
Chapter 11: Thesis Summary and Recommendations for Future Work	158
11.1 Thesis Summary.....	158
11.2 Recommendations for Future Work.....	160
11.2.1 Optimization of Screen-Printed Carbon Nanotubes (CNTs) Field Emitter	160
11.2.2 Optimization of Mesh Structure for Screen-Printed Carbon Nanotubes (CNTs) Field Emitter	161
11.2.3 Fabrication and Field Emission (FE) Characterization CNT Field Emitter Integrated with Mesh	161
11.2.4 Long-term Reliability of the Screen-Printed CNT Field Emitter with Mesh Structure.....	162
Author's Publications.....	164
References.....	165

List of Figures

Figure 2 - 1: 10 years of global satellite industry revenue from 2007 to 2016 [22]	5
Figure 2 - 2: Percentage breakdown of operational satellite by functions in year 2013 [22]	6
Figure 2 - 3: Categorization of satellites by mass, cost, and response time [25]	7
Figure 2 - 4: Historical launches and projected future market potential of small satellites from year 2010 until 2023	7
Figure 2 - 5: Historical percentage breakdowns of small satellites by functions [26]	8
Figure 2 - 6: Basic Components of Satellite Communication system [28]	9
Figure 2 - 7: Frequency and power capabilities of MVED and SSPA [37]	12
Figure 2 - 8: Illustration of the fundamental variance between: (a) SSPA, and (b) MVED [38]	14
Figure 2 - 9: Schematic diagram of a typical TWTA [53]	21
Figure 2 - 10: Schematic diagram of beam-wave interaction in TWTA [53]	23
Figure 2 - 11: Reduction in the size of TWTA from late 1980s [38]	25
Figure 2 - 12: Schematic diagram of FE phenomenon	29
Figure 2 - 13: Current/Voltage ranges of thermionic and FE cathodes in TWTA [69]	32
Figure 2 - 14: (a) Schematic diagram, and (b) SEM image of a Spindt-type electrode [70] ...	33
Figure 2 - 15: SEM image of several possible failure modes of the Spindt cathode [73]	34
Figure 2 - 16: Utsumi's relative figure of merit of emitters with (a) rounded whisker, (b) sharpened pyramid, (c) hemi-spheroidal, and (d) pyramidal [19]	36
Figure 2 - 17: Schematic models of (a) SWCNT and (b) MWCNT; as well as the TEM images of (c) SWCNT [88] and (d) MWCNT [87]	40
Figure 2 - 18: (a) Various CNT shapes; and their associated (b) electric field strength at CNT apex [94]	43

List of Figures

Figure 2 - 19: Electrical field (lines) distribution of (a) CNT array, and (b) individual CNT [97].....	44
Figure 2 - 20: Electrical field strength at CNT apex as a function of the average density of CNT for a CNT at a height of 8 μm [97]	44
Figure 2 - 21: Schematic diagram of a CVD setup [98]	46
Figure 2 - 22: SEM images of CNT grown on catalyst dots (a) Patterned CNT, and (b) Individual CNT pillar [100]	46
Figure 2 - 23: Schematic diagram of a sandwich-structure catalyst layers.....	48
Figure 3 - 1: Schematic diagram of PH-SWS [110]	51
Figure 3 - 2: Motivation roadmap for this PhD study.....	52
Figure 4 - 1: Schematic diagram of: PH-SWS TWTA under (a) and (b) orthogonal view, (c) cross-sectional view, and (d) PH-SWS under orthogonal view.....	55
Figure 4 - 2: (a) Electron ‘bunching’ in TWT; (b) Input and output signals of PH-SWS TWTA operated under 10 mA beam current; electric field distribution on PH-SWS (c) before, and (d) after amplification	57
Figure 4 - 3: Signal Gain of PH-SWS TWTA at various beam current values	58
Figure 4 - 4: Elliptical cross-section of the electron beam at (a) 10 mA, (b) 20 mA, and (c) 40 mA electron beam current; as well as (d) y-z plane of 40 mA electron beam.....	60
Figure 4 - 5: (a) Schematic diagram of BFE, (b) Electron Trajectory, and (c) Electric field distribution in both BFE and TWTA	64
Figure 5 - 1: SEM images of PECVD-grown CNTs: Cross-sectional view of as-grown CNT film at (a) x4000, and (b) x25000 magnification; plane view of (c) as-grown, and (d)	

List of Figures

densified PECVD film at x1000 magnification; plane view of (e) as-grown, and (f) densified PECVD film at x7000 magnification.....	68
Figure 5 - 2: TEM images of PECVD-grown CNTs at (a) lower magnification, and (b) higher magnification	69
Figure 5 - 3: (a) FE Characteristics, and (b) FN plot of as-grown and densified PECVD-grown CNT films	70
Figure 5 - 4: Simulated Electric Field: Orthogonal view of (a) as-grown, and (b) densified CNT film; Cross-sectional view of (c) as-grown, and (d) densified CNT films; (e) localized electric field on the CNT tips.....	71
Figure 5 - 5: Synthesis process of the 3D CNT network	73
Figure 5 - 6: SEM images of: Secondary CNTs under (a) cross-sectional, and (b) plane view; primary CNTs under (c) cross-sectional, and (d) tilted view.....	75
Figure 5 - 7: SEM images of: (a) densified CNTs; 3D CNTs under (b) plane view, and (c) cross-sectional view	76
Figure 5 - 8: TEM images of: (a) & (b) primary CNTs, (c) & (d) 3D CNTs, (e) & (f): primary-secondary CNTs interface.....	78
Figure 5 - 9: (a) FE measurements, (b) FN plots of secondary CNTs, as-grown primary CNTs, densified primary CNTs, and 3D CNTs	79
Figure 6 - 1: SEM images of pre-deposited catalyst TCVD-grown CNTs: (a) Cross-sectional view of CNT film; plane view of (b)as-grown, and (c) densified CNT film at $\times 500$ magnification; (d) Individual CNT cluster	86
Figure 6 - 2: TEM images of pre-deposited catalyst TCVD-grown CNTs: (a) Closed-ended CNT tip, (b) CNTs showing tube diameter of ~ 47 nm	86

List of Figures

Figure 6 - 3: (a) FE Characteristics, and (b) FN plot of pre-deposited catalyst TCVD-grown and PECVD-grown CNT films	88
Figure 6 - 4: (a) FE Measurements, and (b) FE current density at 7 V/ μm applied field for as-grown/densified TCVD-grown CNT film	89
Figure 6 - 5: (a) Raman Spectrum, and (b) FE Current Density and I_d/I_g ratio, of TCVD-grown CNTs at different CNT aspect ratios	90
Figure 6 - 6: SEM images of (a - b) pre-deposited catalyst, and (c - d) floating catalyst-grown CNTs of ~ 11 and ~ 16 μm heights.....	92
Figure 6 - 7: Raman spectra of both pre-deposited and floating catalyst-grown CNTs	93
Figure 6 - 8: (a) FE measurements, and (b) FN plots of both pre-deposited and floating catalyst-grown CNTs (~ 11 and ~ 16 μm height).....	94
Figure 6 - 9: TEM images of floating catalyst-grown CNTs.....	95
Figure 6 - 10: CNT growth mechanisms of (a) pre-deposited, and (b) floating catalyst-grown CNTs	96
Figure 6 - 11: Simulated electric field on CNTs with (a), (c): Similar tip dimensions with CNT body; (b), (d): Enlarged tips.....	97
Figure 7 - 1: Schematic diagram of CNTs grown in Si/SiO ₂ structure	103
Figure 7 - 2: SEM images: Cross sectional view of CNTs grown on (a) Si, and (b) SiO ₂ substrates at 860 °C growth temperature; plan view of CNTs grown on Si substrates at (c) 790 °C, and (d) 860°C growth temperatures; (e) SEM image, and (f) XPS Spectra of FeSi ₂	105
Figure 7 - 3: TEM images of CNTs grown on (a-b) Si; and (c-d) SiO ₂ substrates at 820 °C growth temperature.	106

List of Figures

Figure 7 - 4: CNT diameters distribution on Si and SiO ₂ substrates at 820 °C growth temperature	108
Figure 7 - 5: Raman spectroscopy of CNTs grown on (a) Si, and (b) SiO ₂ substrates; (c) I _d /I _g ratios of CNTs grown on Si and SiO ₂ substrates	108
Figure 7 - 6: CNT growth rates on Si and SiO ₂ surfaces; CNT growth rate reported by Bai et al., on Si surface, at varying growth temperatures [168]	109
Figure 7 - 7: Mechanism of the selective growth of CNTs on Si substrates	112
Figure 7 - 8: SEM Images: (a): Plane view of CNT bundles; (b) plane view, and (c): cross-sectional view of single CNT bundle. Raman map: (d) 1339 – 1444 cm ⁻¹ (D-band) and (e) 1575 – 1577 cm ⁻¹ (G-band).....	113
Figure 8 - 1: Schematic diagram of vertically-aligned CNTs and random-growth of CNTs	116
Figure 8 - 2: (a) Fabrication Process of CNT Samples; (b) Schematic diagram of (i) Sample A, (ii) Sample B, and (iii) Sample C.....	118
Figure 8 - 3: SEM images of: (a), (b) Freestanding CNT bundles (Sample A); (c), (d) CNT bundles grown in 2 µm diameter SiO ₂ pits (Sample B); (e), (f) CNT bundles grown in 0.5 µm diameter SiO ₂ pits (Sample C).....	120
Figure 8 - 4 (a-d): TEM images of CNTs grown by floating catalyst TCVD technique (790 °C selective growth condition).....	122
Figure 8 - 5: (a) FE measurement of Sample A	124
Figure 8 - 6: FE measurement of Sample B at varied separation distances between SiO ₂ pits	124
Figure 8 - 7: (a) FE measurements, and (b) Electric field to achieve 1 A/cm ² FE current density, for Sample C at varying inter-pit separation distances	125

List of Figures

Figure 8 - 8: (a) FE measurements, and (b) FN plots of Samples A, B, and C at the same inter-pit separation distance of 4 μm	126
Figure 8 - 9: Emission current of CNT samples over ~1 hour continuous emission under different applied field: (a) Sample A (50 V/ μm), (b) Sample B (21 V/ μm), and (c) Sample C (24 V/ μm)	128
Figure 9 - 1: Fabrication process and dimensions of screen-printed CNT field emitter.....	134
Figure 9 - 2: SEM images of screen-printed CNTs under (a) 50000 $\times$ magnification, and (b) 100000 $\times$ magnification (inset: TEM image of single CNT).....	136
Figure 9 - 3: Raman Spectra of screen-printed CNTs.....	136
Figure 9 - 4: FE Measurements of: (a): Pristine CNTs, and CNTs with ITO/Ni additives (2 $\times$ 4 mm dimension); and (b) CNTs field emitter (with additives) of varying dimensions.....	137
Figure 9 - 5: Repeated FE Measurements on CNT field emitter (with additives) of (a) 0.5 $\times$ 1 mm, (b) 1 $\times$ 2 mm, and (c) 2 $\times$ 4 mm	138
Figure 9 - 6: Simulated electric field on CNT emitter of various dimensions (along w-direction as presented in Figure 9 - 1)	139
Figure 10 - 1: Schematic diagrams of plane anode measurement system and CNT field emitter with mesh structure.....	142
Figure 10 - 2: Simplified models: Orthogonal and cross-sectional views of CNT emitters with (a) & (c): plane anode; (b) & (d): hexagonal mesh, respectively.	143
Figure 10 - 3: Potential and electric field distribution on CNT emitters with (a) & (c) plane anode; and (b) & (d) hexagonal mesh, respectively	144

List of Figures

Figure 10 - 4: Plane view schematic diagrams of: RH mesh (a) Single RH opening, (b) CNT field emitter with RH mesh; EH mesh: (c) Single EH opening, (d) CNT field emitter with EH mesh (EH2)	145
Figure 10 - 5: Simulated electric field on CNT emitters with plane anode, RH mesh, and EH meshes: (a) along x-axis, (b) at $x = 0$	147
Figure 10 - 6: Electron trajectories of CNT field emitter with: (a) plane anode, and (b) hexagonal mesh (RH: 50 μm).....	148
Figure 10 - 7: Current emitting behaviour of CNT field emitter with plane anode, RH mesh (RH: 50 μm), and EH meshes: (a) Current emitted from CNT emitter, and current escaped from mesh structure; (b) Percentage breakdown of electrons escaped from the mesh and collided on the mesh	149
Figure 10 - 8: Schematic diagrams of RH meshes: (a) RH:30 μm , (b) RH:80 μm , (c) RH:100 μm , and (d) RH:150 μm	151
Figure 10 - 9: Simulated electric field on CNT emitters with plane anode and RH meshes: (a) along x-axis, and (b) at $x = 0$	152
Figure 10 - 10: Current emitting behaviour of CNT field emitter with plane anode and RH meshes: (a) Current emitted from CNT emitter, and current escaped from mesh structure; (b) Percentage breakdown of electrons escaped from the mesh and collided on the mesh.....	153
Figure 10 - 11: (a) Schematic diagram of BFE, (b) Potential Distribution, (c) Electron Trajectory, and (d) Electric field distribution in BFE and TWTA	155
Figure 10 - 12: (a) Input and output signals of PH-SWS TWT, (b) elliptical cross-section of the electron beam, under 20 mA electron beam, 60 $\times$ 200 μm rectangular electron emitter.	156
Figure 11 - 1: Schematic diagram of: (a) Screen-printed CNTs and mica spacer assembly, and (b) assembly of fabricated mesh with mica spacer and screen-printed CNTs.....	162

List of Tables

Table 2 - 1: Satellite frequency bands and the associated applications [30]	9
Table 2 - 2: Comparison between MVED and SSPA [39]	14
Table 2 - 3: Advantages, disadvantages, and performances of SSPA and MVED in satellite applications [51].....	19
Table 2 - 4: Issues related to hot cathode and the solutions by cold cathode [45, 57, 61].....	30
Table 2 - 5: Reported FE properties of various materials	38
Table 2 - 6: General Properties of CNT [90]	41
Table 2 - 7: Emission Characteristics of CNT in the state-of-art	49
Table 4 - 1: Dimensions of the PH-SWS in Micrometre	56
Table 4 - 2: Simulation Parameters of PH-SWS TWTA	56
Table 4 - 3: Degree of Rotational Tolerance of Field Emitter at Varied Electron Beam Current Values	62
Table 5 - 1: Sample Labelling of 3D CNT network	74
Table 5 - 2: FE properties of primary, secondary, and 3D CNTs	81
Table 6 - 1: CNT height at various growth duration.....	89
Table 6 - 2: FE Current Density and Field Enhancement Factors of both Pre-deposited catalyst and Floating Catalyst-grown CNTs	94

Table 8 - 1: Sample specifications	118
Table 8 - 2: FE properties of Samples A, B, and C at 4 μm inter-pit separation distance (Summarized).....	127
Table 10 - 1: Mesh Label and Geometrical Specifications of RH and EH Meshes.....	145
Table 10 - 2: Mesh Label and Geometrical Specifications of RH Meshes.....	151

List of Abbreviations

1D	One-Dimensional
Al	Aluminium
Al ₂ O ₃	Aluminium Oxide
BFE	Beam Forming Electrode
C ₂ H ₂	Acetylene
CNT	Carbon Nanotube
Co	Cobalt
CVD	Chemical Vapor Deposition
EH	Elongated Hexagon
FE	Field Emission
Fe	Iron
FN	Fowler-Nordheim
H ₂	Hydrogen
MVED	Microwave Vacuum Electron Devices
MWCNT	Multi-Walled Carbon Nanotubes
NH ₃	Ammonia
Ni	Nickel
PECVD	Plasma-Enhanced Chemical Vapor Deposition

List of Abbreviations

PH-SWS	Planar Helix-Slow Wave Structure
PIC	Particle-In-Cell
RF	Radio Frequency
RF	Radio Frequency
RH	Regular Hexagon
SEM	Scanning Electron Microscope
Si	Silicon
SiO ₂	Silicon Oxide
SSPA	Solid State Power Amplifiers
SWCNT	Single-Walled Carbon Nanotubes
TCVD	Thermal Chemical Vapor Deposition
TEM	Transmission Electron Microscope
Ti	Titanium
TiN	Titanium Nitride
TWTA	Traveling Wave Tube Amplifier
VLSI	Very-Large-Scale Integration

Chapter 1: Introduction and Overview

The evolution of satellite communication took place in 1957 when the Soviet Union launched the first artificial satellites in human history, SPUTNIK 1 and 2. A year later, the United States of America (USA) launched its first satellite, EXPLORER, in January 1958. Later on that same year, the USA launched its second satellite, SCORE, which appeared to be the world's first communication satellite. Since the launch of SCORE, a series of communication satellite missions were launched in the 1960s. In fact, numerous communication satellites were successfully launched for television broadcast [1], radio communication [2], and telecommunication [3] purposes within that decade [4].

In this modern era, communication satellite has occupied a significant percentage breakdown among successfully launched satellites. Furthermore, as a result of globalization, exponential rise in demand for data transmission, broadband connections, and real-time broadcasting has been predicted for the next decade. Hence, in order to cater to this pressing demand, high speed data transmission and broad data coverage area are crucial to support such trend. As for high speed data transmission, the usage of high frequency data transmission (Ka-band) has been proposed to relieve the congestion experienced in the present frequency band (Ku-band) [5]. Nevertheless, the satellite industry shall continue to remain a challenge among nations with limited budget and technologies in space. Thus, in the attempt to lower the benchmark in entering the satellite industry, small satellites (micro-, nano-, picosatellite) have been introduced. In fact, the sophisticated and stand-alone characteristics of these modern and petite satellites have enabled organizations with moderate technological capability to make their first move in entering the industry. As a result, the data coverage area has been estimated to expand due to the lowered budget-benchmark within the communication satellite industry.

Nevertheless, the main challenge in using both approaches (Ka-Band and small satellites) to meet the increasing demand is the limitation of small satellites. The present development in high frequency small satellite technologies has remained unsatisfactory. One reason for this is due to the absence of miniaturized signal transmission devices that can operate in high frequency ranges [6]. Due to this limitation, the use of small satellites is rather uncommon for commercial communication. As such, the development of a miniature signal transmission device with high frequency capabilities is indeed essential, especially in the attempt to merge both approaches (Ka-Band and small satellites) as the solution for future data transmission.

As predicted in Moore's law, the progress in solid-state transistors would undergo an exponential pace with transistors that have a factor of two, smaller, faster, and cheaper for every 18 months [7]. Nonetheless, as the devices are scaled down to nanometre levels, possible reliability issues can be foreseen [8]. Hence, in order to sustain the continuity of Moore's law, NASA has proposed that vacuum electronic device as a possible solution. Due to the high electron mobility in vacuum electronic device, it requires fewer devices per chip to carry out an operation similar to solid-state transistors, which appear to be a viable alternative for the continuity of Moore's law [9].

Among the various vacuum electronic devices available, the Traveling Wave Tube Amplifiers (TWTAs) have received much attention due to its high operation frequency and wide bandwidth [10], [11]. As for high speed Ka-band communication, a small diameter ($< 1\text{mm}$) of Slow-Wave Structure (SWS) is needed [12], thus driving increased demands for miniaturized TWTAs. Besides, in a study reported by our research group, a Planar Helix-SWS (PH-SWS) has been proposed to be fabricated by using silicon-based microfabrication techniques [13]. Furthermore, in the attempt to incorporate sheet beam into the PH-SWS TWTAs, the design of a sheet-beam electron gun is generated [14]. From the sheet-beam design, operation with a small-sized field emitter, which is capable of emitting high current density

(few hundreds mA/cm² to few A/cm²), is required to realize the application of PH-SWS in TWTA [15].

Therefore, in order to enable the microfabrication of vacuum electronic devices, miniaturized and high current density field emitters with high growth selectivity are demanded. In fact, many types of one-dimensional (1D) nanostructure field emitters have been reported in the state-of-the-art, such as diamond nanowire [16], zinc oxide nanowire [17], silver nanowire [18], and Carbon Nanotubes (CNTs) [8], to name a few. These nanostructures display promising FE characteristics for a possible application in the modern vacuum electronic devices. Among the reported nanostructures, CNTs have exhibited rather outstanding FE properties resulting from their unique atomic structure [19]. Nonetheless, due to various technical issues, such as screening effect [20] and weak substrate adhesion [21], CNTs have portrayed limited feasibility for the actual application in miniaturized TWTAs. Hence, a comprehensive study on the design, the synthesis, and the fabrication of CNT field emitter for its application in TWTAs is called for.

With that, as for this PhD study, the synthesis and the fabrication of CNT field emitter for TWTAs are divided into a few major sections. As such, Chapter 4 depicts the simulation of Particle-In-Cell (PIC) that was carried out on miniaturized TWTA to gain preliminary comprehension on the effect of electron beam current upon TWTA signal. Next, an FE comparative study was performed to determine the most suitable CNT growth technique in order to fabricate high FE current density field emitter. The FE comparative study is thoroughly discussed in Chapters 5 and 6. After that, the fabrication of CNT field emitter using the selected growth technique is reported in Chapters 7 and 8. Furthermore, in the attempt to explore the possibilities of achieving higher FE current density via CNTs, screen-printed CNT with microfabricated mesh is reported in Chapter 9. Finally, based on the retrieved FE behaviour

exerted upon the fabricated CNT field emitter, PIC simulation was re-performed on miniaturized TWTA so as to speculate the possible behaviour of TWTA under such CNT field emitter in Chapter 10.

Chapter 2: Literature Review

2.1 Basic Operations and Development Trends in Satellite Communication

As mentioned in Chapter 1, a progressive trend has been noted on the development of global satellite industry, especially for communication applications. Among the launched satellites, the usage of small (1 – 50 kg) satellites has exhibited somewhat large potentials due to its favourable economic viability. On the other hand, commercial communication in Ka-Band has drawn much attention due to the high-speed data transmission that has further attributed to its high frequency range. Hence, this section depicts the development of small satellites, along with its feasibility in operating the Ka-Band.

2.1.1 Overview and Progressing Trend

The ever-increasing demand in data transmission, the real-time broadcasting, and the broadband connections have driven the global market to rapidly expand the satellite industry over the past decade. Furthermore, based on a market research carried out by BRYCE Space and Technology, progressing from year 2007 until year 2016, the global satellite industry revenue had experienced more than double the increment, from \$122 billion in 2007 to a whopping \$261 billion in year 2016, as portrayed in Figure 2 - 1 [22].

Figure 2 - 1: 10 years of global satellite industry revenue from 2007 to 2016 [22]

In addition, the same report claims that the total number of operational satellite was estimated to be 1459 in year 2016. Out of all the operational satellites, it was reported that 35% of the operating satellites are used in commercial communication (Figure 2 - 2). The usage of satellites in commercial communication has highly outnumbered other functional operations, such as scientific, military, and remote sensing functionality. Therefore, the next few years have been expected to witness an escalating demand for high data transmission rate [23]. Therefore, commercial communication satellite has been predicted to play a significant role in the future satellite industry.

Figure 2 - 2: Percentage breakdown of operational satellite by functions in year 2013 [22]

Furthermore, in order to categorize these satellites, the satellite community has fixed a standard to distinguish between small and large satellites based on their masses, as illustrated in Figure 2 - 3. Small satellites are referred as satellites lighter than 1000 kg. Besides, Figure 2 - 3 shows that smaller satellites require lower launching cost and shorter response time for full-fledge operation [24]. Due to this advantage of small satellites, an increasing demand has been noted in the usage of small satellites in various communication systems. Furthermore, a renowned satellite research centre, Spaceworks, has reported the usage of small satellites since

year 2010, along with its estimated usage for the next few years. The report further states that the global usage volume of small satellites (1 – 50 kg) can be speculated to be 320 across the globe, with full market potential of 460 small satellites in year 2023 (Figure 2 - 4).

Figure 2 - 3: Categorization of satellites by mass, cost, and response time [25]

Figure 2 - 4: Historical launches and projected future market potential of small satellites from year 2010 until 2023

Despite of the speculated potential in small satellites, the present usage of small satellites in communication is still at an unsatisfactory level. Based on the same report published by Spaceworks, small satellites are commonly employed for earth observations,

scientific researches, technological development, and communication functions, especially from year 2009 until 2016. Among the available small satellites, only 6% have been utilized for communication applications [26]. This could be due to the escalating demand in high frequency, high speed, and broader communication, where small satellites do not possess the capability to achieve such features. More details of the satellite communication system are provided in the next section.

Figure 2 - 5: Historical percentage breakdowns of small satellites by functions [26]

2.1.2 Satellite Communication System and Operation Bands

An outline of the satellite communication system is portrayed in Figure 2 - 6. In a typical satellite communication system, the electromagnetic signal is first initiated from the originating ground station (or uplink) to the receiving antenna mounted upon the satellite. Next, the satellite transforms the received signal to the destination ground station (or downlink) via

transmitter. The signal is often amplified by an amplifier before transmission takes place. Some commonly types of amplifiers used are often based on solid-state or vacuum electronics technologies [27].

Figure 2 - 6: Basic Components of Satellite Communication system [28]

The operation of satellite communication is restricted by frequency bands, as regulated by the International Telecommunications Union (ITU), a sub-organization of the United Nations (UN). Due to such regulations, the frequency range that is available for satellite communication becomes limited. In fact, several other similar services also tend to use the same frequency ranges. Hence, the aspect of efficiency appears to be crucial in utilizing the permitted frequency range for any application [29]. With that, Table 2 - 1 summarizes the assigned frequency bands, along with the corresponding services.

Table 2 - 1: Satellite frequency bands and the associated applications [30]

Band	Frequency (GHz)	Range	Applications/Services
L-	1 – 2		Global Positioning System (GPS) and mobile phone
S-	2 – 4		Weather radar and ship radar

C-	4 – 8	Full-time satellite TV networks
X-	8 – 12	Weather monitoring, military air traffic and maritime vessel, traffic control, and defence tracking
Ku-	12 – 18	Direct broadcast satellite service
Ka-	26 – 40	High-resolution detection and targets on military aircraft

Due to the high flow rate of data, the present satellite bands in communications appear to be overloaded. This is because; both civil and commercial providers of cellular phones, instantaneous streaming, and data communications have all exerted unbearable strain on the available bandwidths, thus causing severe congestion amongst the bands. As such, commercial owners have been pressing the authorities to free up other bands within the electromagnetic spectrum so as to relieve the congestion. As for high speed data transmission, a higher frequency band is required for an accelerated rate of data transmission. Furthermore, in order to cater to the need for speedy transmission, high frequency Ka-band is used as the spectrum for enhanced data transmission [31].

In addition, so as to support the operation of small satellites with high speed Ka-Band frequencies, sophisticated devices that are capable of operating in high frequencies in harsh space conditions are in need. In fact, the possible devices that could be utilized for this application are elaborated in the following section. Meanwhile, Figure 2 - 6 depicts the amplification of electromagnetic signal before it is transformed to the destination at ground station (downlink).

2.2 Signal Amplifiers in Satellite Communication

As illustrated in Figure 2 - 6, satellite communication is operated in a manner where the Radio Frequency (RF) signal is transmitted onto the launched satellite. Following that, the

RF signal is amplified by a signal amplifier, and transmitted back to the downlink at earth. This section presents the development of signal amplifiers, along with their respective feasibility in satellite application.

2.2.1 Historical Development in Signal Amplifiers

In the advent of electronic computers, information processing was performed via electromechanical relays [32]. This processing technology was then advanced when the relays were substituted by the newly-invented vacuum tube in 1904 [33]. The development of vacuum electronics was pioneered by the initial discovery of thermionic emission phenomenon in 1873 [34]. Nonetheless, the usage of vacuum electronics in signal rectification took place only in 1904, when two renowned scientists, A., Fleming and De Forest, introduces vacuum-based diode and triode, respectively [33]. In fact, the real commercialization of Microwave Vacuum Electron Devices (MVED) began to take place during the early 1900s, which had been then assimilated into both consumer and industrial products in the 20th century.

In opposed to the progress of vacuum electronics, the solid-state electronics had occupied a shorter timeline in the historical development related to signal-amplification technology. In fact, the initial and historical solid state transistor was demonstrated exactly on an afternoon in December 23rd 1947 by Brattain and H. R., Moore to their colleagues in Bell Labs [35]. It then turned into a stepping stone for the emerging trend of Solid State Power Amplifiers (SSPAs), which had successfully ignited to replace the existing MVED. As a result, the annual production of MVED took a gradual deterioration and this further slumped due to the rapid emergence of SSPA in the 1960s [36].

With the progress of SSPA, Gordon Moore, the CEO of Intel, envisioned the VLSI development trend, which is also known as Moore's Law [7]. As stated in the Moore's law, the development in solid-state transistors goes through an exponential pace with transistors gaining

a factor of two smaller, faster, and cheaper in every 18 months [8], [32]. Nevertheless, as these devices are scaled down to nanometre levels, some potential issues related to reliability can be foreseen. At nanometre scales, the electrical insulation between the devices becomes a hurdle due to the possible electron tunnelling [8]. Hence, in order to sustain the continuity of Moore's law, NASA has projected the vacuum electronic device as a viable solution. As vacuum electronic device involves drifting of electron beam in vacuum atmosphere, high electron mobility is generated, which supports operation at high speed. Thus, as a result, fewer devices per chip are required to perform similar operation as the solid-state transistors [9].

Figure 2 - 7: Frequency and power capabilities of MVED and SSPA [37]

Figure 2 - 7 displays the frequency and the power capabilities of both MVED and SSPA. The figure further portrays that the operation frequency of satellite communication amplifiers falls within the region of technology overlap. This means; both MVED and SSPA are capable of operating in this frequency range. Nonetheless, within the context of Ka-Band satellite operation, more factors need to be weighed in when comparing the aspect of feasibility between SSPA and MVED in a high frequency Ka-Band operation. Besides, as the space environment involves fluctuating temperature conditions and high vacuum environment, these factors have

to be considered when selecting the most suitable device. The comparison between SSPA and MVED is discussed in the next section.

2.2.2 Comparison between SSPA and MVED

Despite of being cost-effective, small-sized, and other associated advantages of SSPA, the use of MVED appears to be the preferred device in several specified applications. Furthermore, in comparing between vacuum and solid-state electronics technologies, it is, first, essential to comprehend to basic operation, as well as the physical variances between SSPA and MVED. Hence, as presented in Figure 2 - 8(a), SSPA, basically, operates on the electron flow in the base (for Bipolar Junction Transistor) or at the gate (for Field-Effect Transistors). Meanwhile, in a typical SSPA, the alternating-current (AC) voltage at low current is applied to the base (or gate) between the collector and the emitter (or source and drain for Field-Effect Transistors). The electron flow is further sustained by the voltage applied across the base (or gate). Besides, the power gained by the device is based on the frequency modulations upon the emitter-base or the source-drain current. On the contrary, MVED operates on electron beam that is emitted from the cathode into an evacuated region. In addition, the electron stream is sustained by the inertia of the electrons itself. Based on Figure 2 - 8(b), the microwave signal is inserted through the inlet-end of the interaction circuit. After that, the electric field of the microwave radiation interacts with the electron beam, where the kinetic energy from the electron beam gets transferred to the microwave to form more intense microwave field power [38]. Table 2 - 2 presents the comparison between general SSPA and MVED.

Figure 2 - 8: Illustration of the fundamental variance between: (a) SSPA, and (b) MVED [38].

Table 2 - 2: Comparison between MVED and SSPA [39]

	Microwave Vacuum Electron Device (MVED)	Solid State Power Amplifier (SSPA)
Heat generation	Localized heat generation	Heat generated within the device
Thermal tolerance	250 °C and above	Below 30 °C
Electron movement	Collision-less movement in evacuated region	Collisional movement in crystalline structure
Operation frequency	Operates with frequency up to 460 GHz	Operates with maximum frequency of 40 GHz
Conventional fabrication method	Mass-produced with micro-fabrication techniques	Individually-produced with mechanical fabrication techniques

Besides, in a typical MVED, heat is usually generated at the collector plate via collision among the high speed electrons. This generation of heat should not be confused with the thermionic emission of cathode, where heat is applied intentionally to the sharp-tipped cathode to emit electron. Moreover, localized heating occurs on the collector plate that is placed remotely from the other components (cathode, microwave waveguide, focusing magnets, etc.). In fact, the location of the localized heating region has the potential to minimize issues related to heat-induced damages to other components. Hence, the collector baseplate has a high temperature tolerance of exceeding 250 °C [40]. Nevertheless, when compared to MVED, the heat generation in an SSPA is primarily due to phonon scattering. During the SSPA operation, the electrons lose energy from the phonon scattering in a crystalline structure of the narrow gate (or base). The lost energy is transformed into heat and it is dissipated out through the device. However, heat-induced damages can still occur when the dopants in the micro-fabricated structure migrate at elevated temperatures. Therefore, the collector baseplate must be maintained below 30 °C at all times [41]. In fact, an external coolant or heat sink is required for SSPA due to its sensitivity against thermal factor. In contrast, the sophisticated cooling system is disregarded for MVED due to the remote location of the localized heated component. The cooling mechanisms for both devices are further elaborated in Section 0.

Apart from heat tolerance, the mobility of electron and the resulting frequency-handling capability can distinguish the corresponding performances exerted by both devices. As given in Table 2 - 2, electrons in MVED flow through the evacuated interaction circuit guided by the magnetic field. In opposed to MVED, the electrons in SSPA drift through a nanometre-thin micro-fabricated SSPA. As a result of the varied electron mobility, SSPA and MVED exhibit varying operational frequency ranges. In precise, the MVED can operate at a higher frequency up to 460 GHz, whereas the silicon-based SSPA can only operate at a maximum frequency of 40 GHz.

Due to the limitation of the conventional silicon-based SSPA, alternative materials have been explored to enhance the performance of SSPA. Besides, it is arguable that Gallium Nitride (GaN) possesses the potential of replacing MVED in higher frequency operations [42]. However, the lower resistance of GaN, when compared to silicon, results in lower power loss and heat generation. Such attribute of lower resistance, in fact, allows it to handle over ten times more voltage than the silicon-based devices. Simultaneously, it was reported that GaN devices built on Silicon Carbide (SiC) have significantly improved the aspect of thermal conductivity, in comparison to those fabricated from Gallium Arsenide (GaAs). In other words, GaN devices can operate at higher power densities [43]. Nonetheless, GaN is unable to provide the main advantages of MVED, which is the accommodation of an electron flow without collision and extremely high thermal tolerance ($>250^{\circ}\text{C}$) [44]. As such, it is safe to mention that the emergence of GaN-based SSPA has yet to threaten the present industrial position of vacuum electronics technology.

Despite of the superior characteristics of MVED over SSPA, one of the greatest advantages offered by SSPA over MVED is the established micro-fabrication techniques. The well-established micro-fabrication techniques in silicon-based SSPA enable nanometre-scaled miniaturization and mass production of devices. Furthermore, with the present photolithography scale, the production of nanometre-scaled SSPA components is still highly possible [45]. On the other hand, the main hassle in fabricating MVED is the demand to individually fabricate each component and to assemble in a mechanical manner. Hence, in order to address this particular issue, a concept was proposed by employing the existing micro-fabrication techniques in SSPA to fabricate MVED [9]. The concept of utilizing the established micro-fabrication techniques in MVED fabrication turns to be feasible for most vacuum electronics devices. Hence, due to the well-established silicon-based micro-fabrication

techniques, it is interesting to explore the feasibility of microfabrication techniques in producing MVED.

With that, the advantages and the shortcomings of both SSPA and MVED offer a wide range of options for various applications. As for satellite communication, the option of either SSPA or MVED is still open for argument. In fact, a comparison between SSPA and MVED in satellite communication is discussed in the next section.

2.2.3 SSPA and MVED in Satellite Application

Satellites that operate in space environment experience a somewhat contrasting condition from the conventional atmospheric environment. In the vacuum space, the air pressure is negligible (10^{-12} Torr) due to the low density of air particles. In addition, the outer space also experiences extreme changes in temperature, whereby the sunlight can burn up to $120\text{ }^{\circ}\text{C}$, while the shade may go below $-100\text{ }^{\circ}\text{C}$ [46]. Due to the hostile condition in the outer space, the selection of devices used in the satellite should highly consider the extreme temperature variation with high thermal tolerance. Thus, in the attempt to address such situation, one should first comprehend the fundamental of heat dissipation mechanism in devices.

The heat dissipation mechanism of a typical device is commonly governed by three factors, which are: conduction, convection, and radiation. Nonetheless, more than 50% [47] of heat dissipation is contributed by the convection heat flow. The rate of heat flow by convection on surface can be calculated by using the Newton's Law of Cooling, as shown in Equation (2.1):

$$q_{conv} = hA(\Delta T) \quad (2.1)$$

Where q_{conv} is power transferred (W) by convection, h ($\text{W}/\text{m}^2\text{K}$) refers to heat transfer coefficient, A denotes surface temperature, and ΔT reflects the variance in temperature between surface and ambient. In addition, the heat transfer coefficient(h) ranges from 5 to

25000 W/m²K, depending on the ambient condition. Besides, in order to ensure a continuous air-flow condition, the value of h should exceed that of the still-air condition.

In the event where the density of air particles is extremely low, the heat convection of the device becomes hindered. In fact, the value of h in the outer space is low and negligible primarily due to the low density of air particles. Thus, devices often heavily depend on the radiation route for heat dissipation. Besides, heat generated from the device is first transferred from the heat-generating core to the surface of the device via thermal conduction. Next, the heat on the surface is transferred to the ambient via thermal radiation. Hence, the rate of such heat flow by radiation of a surface is as described in Equation (2.2):

$$q_{rad} = \varepsilon \alpha A (T_1^4 - T_2^4) F_{12} \quad (2.2)$$

Where q_{rad} is power transferred (W) by radiation, ε refers to emissivity, α denotes Stefan-Boltzmann constant (5.67×10^{-8} W/m²K⁴), F_{12} is defined as view factor, whereas T^1 and T^2 are temperature values for surface and ambient. In Equation (2.2), the temperature values escalate to the fourth power, thus displaying the minor variation in the temperature values between surface and ambient that could have a significant impact upon heat transfer rate [48].

Furthermore, due to low heat tolerance, it is rather common for Solid State Power Amplifiers (SSPAs) to experience failure in heat induction. However, the operation of SSPA itself has the ability to generate substantial heat. Moreover, as mentioned earlier, more than 50% of heat dissipation is contributed by convection route embedded within the heat dissipation system. Nonetheless, the high vacuum condition in space eliminates the possibility of heat being dissipated via convection. As the rate of heat dissipation declines by more than 50%, a hefty amount of heat is trapped in the device, thus leading to failure in thermal induction within these SSPA devices [49].

On the contrary, failure of thermal induction is rather uncommon in MVED. Its high thermal tolerance and remote location of the heated region (electron collector) make MVED less susceptible to thermal-induced damages. Furthermore, the heat dissipation rate by radiation can increase in a rather rapid manner with slight temperature increment in the collector, as shown in Equation (2.2). Nevertheless, other sources of failures are still possible in MVED, primarily due to interface disjoint, defect in materials, or even poor workmanship [50]. Therefore, the differing failures in the mechanisms of both SSPA and MVED point towards varied benefits and shortcomings. For better comprehension, both the characteristics and the performances of SSPA and MVED in satellite applications are summarized in Table 2 - 3.

Table 2 - 3: Advantages, disadvantages, and performances of SSPA and MVED in satellite applications [51]

Solid State Power Electronics (SSPA)		Microwave Vacuum Electron Devices (MVED)
Mass	Light	Bulky
Cost (per device)	Low	Expensive
Power consumption	Requires low voltage (5-10 V DC)	Requires high voltage (kilo-Volt)
Output power	Low	High
Efficiencies	14% in S-band, 46% in C-band, and 1% in Ku-band	6% in S-band, 18% in C-band, 62% in Ku-band, and 14% in Ka-band
Operational hours	92 million	211 million

Generally, SSPA displays higher efficiencies at low frequency bands (S- and C-bands). Nonetheless, the low efficiency (1%) of SSPA upon operating in Ku-Band reflects its

inferiority in operations with high frequency. Meanwhile, MVED exhibits higher efficiencies in high frequency bands (62% in Ku-band and 14% in Ka-band). Therefore, due to the high efficiencies in both Ku- and Ka-Bands, MVED is often selected for operations that require high frequencies (Ka-Band). The exceptional attributes projected by MVED, which are high efficiency in high frequency operation, high thermal tolerance, and longer operational hours, defeats SSPA, thus emerging as the more desired device. However, despite of the superiority claimed by MVED over SSPA, the bulkiness and the higher cost of MVED have remained unsolved. With that, the potential of miniaturization in TWTA is further discussed in the next section.

Due to the high reliability and capabilities in operating at high frequency condition, TWTA has been widely employed in transmitting satellite signals among MVEDs. In addition, the operational lifetime of a typical TWTA is beyond 200 million hours. Besides, TWTA can deliver a device with efficiency as high as 62% when operating in high frequency Ku-band [51]. The details of the fundamental operating mechanisms and the capabilities of TWTA are elaborated in the following section.

2.2.4 Traveling Wave Tube Amplifiers (TWTAs)

Among the various MVEDs, some of the most widely used devices for satellite communication are Klystrons and TWTA. Among these devices, TWTA occupies more than 50% of the total sales in MVED market [10]. Moreover, in comparison to TWTA, Klystrons possesses higher efficiency, but unfortunately, narrower bandwidth and lower peak frequency. In fact, the variances in the displayed features can be explained by the fundamental operations of both devices. TWTA uses a synchronous interaction between the electron beam and the electromagnetic wave, along the helix slow wave structure; whereas Klystrons uses the electron ‘bunching’ phenomenon in the designed cavity. In fact, due to the continuous amplification along the tube body, TWTA has been reported to operate with higher signal-to-noise ratio,

when compared to Klystrons. Besides, the cavity-bunching mechanism of Klystrons is limited to its operational bandwidth and peak frequency [52]. Hence, TWTA is often viewed as the ‘last resort’ for high frequency operation in satellite communication.

Figure 2 - 9: Schematic diagram of a typical TWTA [53]

TWTA is referred as a type of MVED that amplifies Radio Frequency (RF) signals via synchronous interaction between an electron beam and an electromagnetic wave. The schematic diagram of a typical TWTA is presented in Figure 2 - 9. As for a typical operation of TWTA, an electron beam is first emitted from an electron gun. The electron beam is then projected into the slow-wave circuit with guidance from the anode and several focusing magnets. In the slow-wave circuit, the electron beam experiences a synchronous interaction with the electromagnetic wave to gain power. Lastly, the spent electron is collected by the collector for dissipation. More details pertaining to the operation and the state-of-the-art TWTA are described in Sections 2.2.4a and 2.2.4b, respectively.

2.2.4a Operation Theory of Traveling Wave Tube Amplifiers (TWTAs)

Beyond doubt, it is significant for both electron beam and electromagnetic wave to experience synchronous interaction for optimal gain. Synchronous interaction is described as matching beam-wave velocities. Since electromagnetic wave has higher velocity than that of

an electron beam, a slow-wave circuit can be applied to reduce the velocity of the electromagnetic wave. This phenomenon is also known as ‘velocity synchronism’. At the velocity synchronism interaction, the lost kinetic energy of the electrons is transferred to the RF wave for power gain.

Such beam-wave interaction and energy transfer can be explained by the ‘bunching’ phenomenon of the electrons in the electric field. During the beam-wave is in contact, the electrons are inserted in various polarity of the electric field. As the electric field appears in the form of a continuous wave, the polarity of each electron depends on when the electron enters the wave propagation region. Hence, electrons that enter into an accelerating polarity speed up and slow down the decelerating polarity. Meanwhile, electrons with varied velocities experience ‘bunching’. The kinetic energy lost during electron ‘bunching’ is transferred to the wave, hence increasing the electromagnetic wave amplitude. Therefore, the main difference of electron ‘bunching’ between TWTA and Klystrons is the ‘bunching’ region. In Klystrons, electron ‘bunching’ occurs in the designed cavity located along the electron beam-propagation path; whereas in TWTA, it occurs along the beam-wave interaction region to gain signal [54].

Figure 2 - 10: Schematic diagram of beam-wave interaction in TWTA [53]

The beam-wave interaction in TWTA is as described in Figure 2 - 10. As illustrated in the figure, the electrons form bunches upon interaction with RF field. Upon entering the electric field region of continuously-alternating polarities, electrons in varied polarities accelerate and decelerate accordingly to form ‘bunches’. Meanwhile, the lost kinetic energy from electron ‘bunching’ is transferred to the wave and exponentially increases the wave amplitude. This is portrayed in the ‘Exponential growth region’ in Figure 2 - 10. When the electrons reach to an extent where they can no longer possible keep those bunches together (spreading out of electron bunches as the beam propagates), the signal gain in the electric field experiences saturation. After that, the signal would begin reducing [53].

Furthermore, as signal gain is a significant parameter in TWTA functionality, it can be expressed in the following approximate form:

$$G(z) = A + B \left(\frac{C\beta_e}{2\pi} \right) z \quad (2.3)$$

where $G(z)$ is power gain along the longitudinal direction (z) of the slow-wave circuit, while A and B are constants of -9.54 and +47.3 dB, respectively, whereas β_e is constant wave number where $\beta_e = \frac{\omega}{v_0}$ [53]. Besides, C is the Pierce gain parameter, where:

$$C = \sqrt[3]{\frac{Z_0 I_0}{4V_0}} \quad (2.4)$$

and Z_0 , I_0 , and V_0 are the circuit impedance, the beam current, and the beam voltage, respectively [55]. Besides, it is important to note that power gain of an idealized TWTA increases simultaneously with electron beam current, as indicated in Equation (2.4). Hence, in order to maximize the signal gain in TWTA, electron emitter of high current is required. The details of the feasible electron emitters used in TWTA are provided in Section 2.3.

2.2.4b Development and Challenges of Traveling Wave Tube Amplifiers (TWTAs)

As for the TWTA in satellite communication, the element of miniaturization is crucial in order to decrease the payload of the launching mission, as depicted earlier. In year 2003, the Northrop Grumman Corporation successfully reduced the size of modern TWTA from the late 1980s, as presented in Figure 2 - 11. In the 1980s, a conventional TWTA has a total length of more than 12 inches. 15 years later, the size of a micro-TWTA has experienced a shrink by a factor of 2.5 in terms of length and diameter. In fact, the projected 'future' length of TWTA in 2003 has been less than 4 inches.

Figure 2 - 11: Reduction in the size of TWTA from late 1980s [38]

In recent years, several significant breakthroughs in TWTA miniaturization have been reported. For instance, Kolwalski et al., reported the fabrication and characterization of miniaturized W-Band TWTA. The fabricated TWTA had a planar slow-wave circuit with a dimension of 68 x 5.8 mm. Besides, the device obtained a linear gain of 27 dB at 55 W of output power when it operated at W-band [56]. Moreover, the slow-wave circuit structure can be further shrunk via micro-fabrication technique. As reported by Wang et al., the helix slow-wave circuit structure was fabricated by using an established micro-fabrication technique that employed solid state electronics fabrication. The resulting dimension of the slow-wave circuit structure ranged between 10^2 and 10^3 μm [57]. Nevertheless, the commercially available TWTA in Ka-band is still bulky [58]. Thus, further exploration in utilizing the micro-fabricated slow-wave circuit structure is crucial so as to achieve smaller-sized TWTA.

In addition, the issue of electron emitter-miniaturization has arisen along with the scaling-down of TWTA. As the size of TWTA has shrunk, a small and compact electron source (or electron gun) is required to fit the slow-wave circuit structure. Hence, in order to retain a similar power gain upon miniaturization, an electron beam with more electrons per unit area is demanded. The current density of an emitter (J) is given in Equation (2.5):

$$J = \frac{I_0}{A} \quad (2.5)$$

where I_0 and A are the electron beam current and the surface area of the electron emitter. By substituting Equations (2.4) and (2.5) into Equation (2.3), the following is obtained:

$$G(z) = A + B \left[\frac{\left(\sqrt[3]{\frac{Z_0 J A}{4V_0}} \right) \beta_e}{2\pi} \right] z \quad (2.6)$$

As depicted in Equation (2.6), when the effective electron emission area (A) decreases, a higher value of current density (J) is required to retain power gain ($G(z)$). Therefore, electron emission with high current density is needed for miniaturized TWTA.

To date, thermionic emitter is the most widely used electron emitter in numerous commercial TWTAs. In a thermionic emission, sharp metallic tips are heated to elevate the temperature ($>1000^\circ\text{C}$) for electron emission [59]. However, several limitations are contained within a thermionic emitter that hinders it from being used in high-frequency and wide-bandwidth operation for modern TWTAs. Thus, an alternative option of field emitter is proposed to overcome these shortcomings. The details of various types of emitters for TWTA operation are discussed in the next section.

2.3 Types of Electron Emitters for Traveling Wave Tube Amplifier (TWTA)

Thermionic emission cathode (or ‘hot cathode’) has been widely used in TWTA due to its high emission density. However, the bulky, heavy, and hot TWTA cathode-based electron gun no longer fulfils the requirement of miniaturized TWTA. As such, an alternative FE cathode (or “cold cathode”) was introduced to fulfil both the miniaturization requirement and the wide voltage/current range of modern TWTA. With that, the following sub-sections present some comprehensive comparisons between thermionic and FE-based cathodes in TWTA.

2.3.1 Thermionic Emission

Thermionic emission refers to the flow of energized electrons from a surface due to thermal effect. The flow of electron is generated by a sufficient supply of thermal energy to the electrons so as to overcome any potential energy barrier. This phenomenon commonly takes place in evacuated space, mainly because a high vacuum condition has lower energy barrier. Apart from vacuum level, the energy barrier of an emission can also be affected by the work function of the emitting materials [60]. The thermionic emission density is represented by Richardson's Equation, as follows:

$$J = AT^2 e^{\frac{-W}{kT}} \quad (2.7)$$

Where T is temperature of the emitter, W is work function of emitter, k is Boltzmann constant, and A is Richardson's constant, expressed as given below:

$$A = \frac{4\pi me k^2}{h^3} \quad (2.8)$$

where h is Planck's constant, m is mass of electron, and e is charge of electron [61].

Due to the high temperature requirement of a thermionic emission cathode, the emitter used is often called 'hot cathode'. A hot cathode is often designed with an array of sharp metallic tips or a filament coated with low work function materials. The most common types of hot cathodes include oxide-coated cathode [62], boride cathode [63], and thoriated filaments [64]. A typical hot cathode can deliver emission current density of up to 3 A/cm² at a temperature of 1400 °C [63]. In fact, the high emission of current density from hot cathodes and the associated high signal gain are some of the main advantages for selecting it as the primary TWTA electron source.

Despite of the high emission density, several disadvantages found in hot cathode do limit its capabilities in modern TWTA usage. One of the main disadvantages of hot cathode is

the high temperature requirement ($>1000^{\circ}\text{C}$) that could lead to technical complications. A direct impact from the high temperature operation is energy efficiency in TWTA operation. Due to heat dissipation from the hot cathode to the surrounding area, the energy efficiency of a hot cathode-based TWTA is often low. Besides, the excessive heat in a hot cathode may cause outgassing that could deteriorate both the device and the emitter. At the same time, the ‘hot’ nature of thermionic emission can also cause thermal drift in the cathode, which fluctuates the emission of electron and its focus [65].

Nevertheless, an alternative that replaces thermionic emission cathode is the FE cathode (or ‘cold cathode’). On the contrary of hot cathode, a cold cathode applies electrical potential energy to overcome the work function of an emitting surface. In an operation that involves cold cathode, high electrical field is applied to ‘pull’ out the electrons. In fact, the term ‘cold cathode’ derives from its operational nature of FE cathode where heating is not required. By utilizing its ‘cold’ operational nature, the thermal-induced complications of a hot cathode can be addressed [66]. The details of FE cathode are portrayed in the next section.

2.3.2 Field Emission (FE)

The FE phenomenon is defined as the emission of electrons due to electrostatic force. The schematic diagram of an FE phenomenon is illustrated in Figure 2 - 12. As a potential difference is applied across cathode and anode, the energized electrons address the potential barrier and are emitted from cathode to anode, based on the direction of the applied electrical field.

Figure 2 - 12: Schematic diagram of FE phenomenon

The initial derivation of FE current was reported in 1928 as Fowler-Nordheim's equation. The emission current is expressed as [67]:

$$I = \frac{aA\beta^2 E^2}{\phi} \exp\left(\frac{-b\phi^{3/2}}{\beta E}\right) \quad (2.9)$$

where a and b are constants with values of $1.54 \times 10^{-6} \text{ A eV V}^{-2}$ and $6.83 \times 10^{-7} (\text{eV})^{3/2} \text{ V cm}^{-1}$, respectively. Next, A is emission area, E is applied electrical field, and β is an enhancement factor that can be defined as the ratio of local electrical field to the applied electrical field [68]. By rearranging Equation (2.9), the following is obtained:

$$\ln\left(\frac{J}{E^2}\right) = \ln\left(\frac{a\beta^2}{\phi}\right) - \frac{b\phi^{3/2}}{\beta E} \quad (2.10)$$

where J is FE current density. A linear Fowler-Nordheim (FN) plot can be obtained by plotting $\ln\left(\frac{J}{E^2}\right)$ against $\frac{1}{E}$. Besides, the field enhancement factor (β) and the work function (ϕ) can be calculated from the gradient and the y-axis interception values of the FN linear plot. For various vacuum electronic devices, the FE cathode (cold cathode) has been identified as a good alternative to thermionic emission cathode (hot cathode). This is because; the room temperature operation of the cold cathode offsets many disadvantages brought upon by hot cathode. The existing issues related to hot cathode and several possible solutions by replacing it with cold cathode are summarized in Table 2 - 4.

Table 2 - 4: Issues related to hot cathode and the solutions by cold cathode [45, 57, 61]

Problem (Hot Cathode)	Solution (Cold Cathode)
Requires bulky heating system	Heating system is not needed
Power loss from the heated cathode	
Thermal-induced outgassing in the device	Room temperature operation
Thermal-induced deterioration of the cathode	
Requires mechanical shutter for instant ON/OFF switching	Instant ON/OFF switching without any additional shutter
Depletion of low work function coating material	Coating material does not deplete due to tip-emission mechanism
Limited current/voltage operating range	Expanded current/voltage operating range

As mentioned earlier, a significant drawback from using the hot cathode in modern TWTA is the requirement of a heating system. In launching a small satellite, the heating system of hot cathode can exert significant load. On the contrary, heating is not needed for a cold cathode operation. This exclusion of high temperature heater for cold cathode lowers the overall mass of the TWTA device [66]. Apart from high temperature operation, another issue in hot cathode is the depletion of low work function coating. Prolonged operational period of hot cathode-based devices may deplete the coating materials, hence resulting in device deterioration. However, a coating material is unlikely to face depletion with cold cathode due to its tip-emitting mechanism [69]. Other advantages of cold cathode over hot cathode include

higher energy efficiency, negligible thermal-induced damages (outgassing, cathode deterioration, etc.), as well as instant ON/OFF switching without additional mechanical shutter.

Apart from the variance in operation temperature, a significant advantage of the cold cathode in TWTA is the current/voltage operation. As depicted in Equation (7), the acceleration voltage and the beam current of a thermionic emitter are related as $I \propto V^{3/2}$ and they operate at a narrow current/voltage range [69]. On the other hand, a cold cathode-based TWTA offers expansion of current/voltage operation range over a factor of 10 [53]. A better illustration of the variances in current/voltage operations is shown in Figure 2 - 13. Moreover, for the same voltage range of 1500 – 5000 V, a hot cathode can only operate at a narrow current range (grey-shaded area), but a cold cathode can operate in a wider range of current value (dark-shaded area) within the same voltage range. This wide operational current range enables TWTA to operate in various bandwidths and power gain (as presented in Equations (3) and (4)). Therefore, a cold cathode emerges as a more suitable electron source in modern TWTA, in comparison to a hot cathode.

Figure 2 - 13: Current/Voltage ranges of thermionic and FE cathodes in TWTA [69]

The selection of a cold cathode (or field emitter) material is a critical factor in dictating the overall performance of TWTA. In applying the advantages of FE in modern TWTA, a field emitter with high current density and a stable emission characteristic is needed. The comparison of various field emitters is presented in the next section.

2.4 Development of Field Emission (FE) Cathode

The advantages of FE over thermionic emission have sparked numerous research interests in the development of FE cathodes (or cold cathodes). One of the first cold cathodes reported is the Spindt-type cathode, patented in year 1973. Nevertheless, technical complications and shortcomings in the Spindt-type cathode have led to frequent failures. As such, varied materials have been explored to overcome the disadvantages in the Spindt-type cathode. The following sub-sections introduce the overview and the technical issues found in the Spindt-type cathodes. Next, a comparison on the properties of FE deriving from a variety of candidate materials for FE is presented and discussed.

2.4.1 Spindt-type Cathode

One of the pioneering studies pertaining to FE cathode (or field emitter) was reported by *Spindt* in 1968. The report claimed that molybdenum spikes were deposited by using selective thin film deposition-and-removal techniques on a rotating substrate. The molybdenum spikes served as the cathode for FE, while a molybdenum ‘gate’ structure was deposited simultaneously to function as the anode for the emission, with alumina being used for cathode-anode dielectric spacing. In fact, the cathode was termed as ‘Spindt-type cathode’, after the inventor, Charles A., Spindt [70]. Next, in year 1973, a patent was filed on a vacuum device that comprised of a continuous array of Spindt-type tips [71]. A better illustration of the cathode structure is presented in Figure 2 - 14. The shaded region in the figure represents the molybdenum thin films and the cathode, whereas the white region denotes the substrate and the dielectric spacer.

Figure 2 - 14: (a) Schematic diagram, and (b) SEM image of a Spindt-type electrode [70]

Due to low power consumption and light weight, the Spindt cathode has a good prospect in space applications. The possible areas of application include electric propulsion, charge control, and electron beam generation [72]. Nonetheless, the reliability of most Spindt cathodes is, unfortunately, rather low. One of the common failure modes of Spindt cathode is unwanted particles attachment. Figure 2 - 15 shows the typical failure modes of Spindt-type cathodes.

Cathode A represents an ideal cathode, while the rest reflect various defective modes. Cathode B and C have undesired particles attached on the tip of the cone and the edge of the gate, respectively. The small thermal capacitance of the particle-tip interface makes the tip less robust and it can easily get burnt-off at high emission current. As for cathode D, the particles form a 'bridge' that connects cathode and anode, thus causing current short during the emission, hence malfunction of the emitter. The undesired particles attachment during the fabrication of Spindt-type cathodes further causes various defective modes in the cathodes [73].

Figure 2 - 15: SEM image of several possible failure modes of the Spindt cathode [73]

Apart from particles attachment, another possible failure mode of the Spindt cathode is due to back-scattering electrons. During an operation of FE cathode, electrons are emitted and accelerated at high electrical field. The energized electrons can possibly hit the residual gas particles in the evacuated region to 'knock out' the valence electrons at the outer orbit of the particles. Due to the high vacuum condition of the surroundings, the energy barrier for the valence electrons to escape from the orbital is lowered. Thus, the gas particles are ionized and

accelerated towards the direction of the emitter. Although the density of air particles is lower at the outer space, both particles and ions that exist in the space environment can potentially deteriorate the cathode. Besides, under the bombardment of positive ions, the cathode degrades and fails over prolonged operational period [9].

From the main failure modes discussed above, some essential properties of good field emitters are summarized. In order to avoid the formation of undesired particles, a field emitter material with ‘clean’ synthesis process is demanded. In precise, residual conductive particles should not form during the synthesis process. Besides, so as to hinder back-scattering of the emitter, two approaches can be applied. First, the voltage used in the emission should be kept as low as possible to ensure that the electrons have less energy and the residual gas particles are less susceptible to ionization from the bombardment of low energy electron. Thus, a field emitter material with high emission density at lower voltage is required. Meanwhile, the second approach applies a field emitter material with a strong and rigid atomic structure. The concrete atomic structure of the emitter can effectively reduce the susceptibility of emitter degradation due to bombardment of positive ions.

Due to the low reliability of the Spindt-type cathode, various types of materials have been explored in the attempt to seek better alternatives for FE-related applications. Aside from exploring new materials, it is important to explore the idealized shape and the dimension of a good field emitter. As such, a whisker-shaped and high aspect ratio emitter had been preferred over a pyramidal-shaped emitter for ideal emission properties [74]. As so to complement the proposal, FE properties of varied high aspect ratio nanostructures (nanorods, fibre, wire, tubes, etc.) have been investigated [75]. The details of these are presented in the next section.

2.4.2 Nanostructured Cathode

The recent advancement of studies about nanostructured materials has sparked vast interests for the application of nanostructures as field emitter. It was reported that the high aspect ratio of nanostructured materials has high potential in FE-related applications. The contribution of high aspect ratio to exceptional FE characteristics can be explained by ‘figure of merit’ or the shape of the emitter. *Utsumi* introduced the figure of merit, which is defined as follows:

$$f_i = \left(\frac{I_i}{I_0} \right) \approx \alpha \left(\frac{r_i}{r_0} \right)^2 \quad (1)$$

where f_i is figure of merit, I_i and r_i are emission current and apex radius of the emitter; I_0 and r_0 refer to emission current and apex radius of an ideal emitter; and α is a function related to the cone angle of the FE, depending on the shape of the emitter. The figure of merit is based on the concept of maximizing current while minimizing both voltage and size of the field emitter. Emitter shapes with higher figure of merit values possess more idealized FE characteristics [74]. The calculated values of f_i for field emitters with various shapes are presented in Figure 2 - 16.

Figure 2 - 16: Utsumi's relative figure of merit of emitters with (a) rounded whisker, (b) sharpened pyramid, (c) hemi-spheroidal, and (d) pyramidal [19]

The figure concludes that an emitter with pyramidal-shape is a non-ideal field emitter. On the other hand, an emitter with high aspect ratio reflects good FE properties, primarily due to its high figure of merit value. As portrayed in Figure 2 - 14, the shape of Spindt-type cathode resembles that of Figure 2 - 16(b), with $f_i=0.18$. Meanwhile, the cylindrical one with high aspect ratio nanostructured materials (nanotubes, nanowire, nanorod, etc.) shares a similar shape of Figure 2 - 16(a). Thus, it can be postulated that the FE behaviour of high aspect ratio nanostructures tends to exhibit high emission density at a low voltage.

Furthermore, as proposed by *Utsumi*'s relative figure of merit theory, one-dimensional (1D) nanostructures with small tip radius and high aspect ratio can be considered as potential candidates for efficient field emitters [76]. In fact, one of the most commonly studied 1D nanostructures is the nanowire structures. For instance, Garry et al., reported the fabrication of zinc oxide nanowires array by using a combination of drop-coating technique. The fabricated zinc oxide nanostructure displayed an FE density of 0.004 mA/cm^2 under low electrical field at $4.8 \text{ V/}\mu\text{m}$, with turn-on field and field enhancement factor (β) of $3.2 \text{ V/}\mu\text{m}$ and 1500, respectively [77]. At the same time, fabrication of silver nanowires for FE purposes was also reported. For example, Jiang et al., reported a synthesis of silver nanowires by using wet chemistry techniques. The resulting silver nanowires array possessed higher current density of 0.98 mA/cm^2 under $12 \text{ V/}\mu\text{m}$ electrical field [78]. The reported FE properties of various materials are further summarized in Table 2 - 5.

Table 2 - 5: Reported FE properties of various materials

Structure	Turn-on Field (V/ μm)	Emission current density (mA/cm ²)	Field Factor (β)	Enhancement Ref.
ZnO Nanowires	3.2	0.004 at 4.8 V/ μm	1500	[77]
Silver Nanowires	3.5	0.98 at 12 V/ μm	427	[78]
Diamond Nanowires	4.2	5.1 at 8.5 V/ μm	NA	[16]
Vertical Graphene Sheets	1.56	39.8 at 6 V/ μm	3892	[79]
Carbon Nanofibers	11	750 at 12.7 V/ μm	400	[80]
Carbon Nanotubes	1.9	850 at 8 V/ μm	1430	[81]

Based on the comparison, the vertical graphene sheet possessed the lowest turn-on field (1.56 V/ μm) as compared to other 1D materials presented in Table 2 - 5. The outstanding FE properties of graphene can be attributed to its graphitic structure, atomic scale thickness, and high aspect ratio nature [82]. In addition, high emission density was reported for carbon nanofibers-based emitters. In fact, an emission density of 750 mA/cm² was reported for carbon nanofibers under electrical field of 12.7 V/ μm . Besides, the high emission density can be attributed to its high aspect ratio structure with small tip radius [83]. Nonetheless, the high turn-on field and the low β value of carbon nanofibers have remained as significant flaws in the overall FE performance.

From the reported studies concerning FE on various 1D materials, Carbon Nanotubes (CNTs) have displayed exceptional FE current density. Moreover, it is interesting to note that the structural advantages of two carbon allotropes (carbon nanofibers and graphene) coexist in CNTs. Besides, CNTs possess graphitic atomic structure that is similar to that of graphene, as

well as small tip radius with high aspect ratio that is similar to carbon nanofiber. The high aspect ratio of CNTs makes a good candidate material as a field emitter, based on Utsumi's relatively figure of merit theory [84]. Unlike the Spindt-type cathode, the strong C-C covalent bond in CNTs offers an effective shielding to cathode degradation caused by back-scattering [65]. In addition, CNTs that are selective and have highly-ordered growth may eliminate the possibility of cathode-anode 'bridge' formation (more details are presented in the latter sections). Thus, it can be postulated that CNTs have high potential to appear as the next generation field emitter.

2.5 Carbon Nanotubes (CNTs) as Field Emitter

Since the advent of CNTs as field emitters [85], the FE characteristics of CNTs have attracted much attention in the research community. Moreover, the outstanding features of FE have positioned CNTs in the limelight among various FE studies. This section discusses the theoretical background, the state-of-the-art, and the possible frontiers of CNTs in FE-related applications.

2.5.1 Introduction to Carbon Nanotubes (CNTs)

The conception of CNTs was first initiated in 1991 by Iijima from NEC [86] as a member of the fullerene family. Varied from the fullerene buckyball structure, CNTs have a long, narrow, and hollow structure. Generally, the walls of CNTs are formed by an atomic layer of thick sheet called graphene. Apart from its single atomic layer of thick walls, CNT walls may also consist of multiple layers of graphene sheets. Hence, CNTs can be categorized as Single-Walled Carbon Nanotubes (SWCNT) and Multi-Walled Carbon Nanotubes (MWCNT) [87]. Figure 2 - 17 illustrates the schematic illustrations, as well as the Transmission Electron Microscope (TEM) images of both SWCNT and MWCNT.

Figure 2 - 17: Schematic models of (a) SWCNT and (b) MWCNT; as well as the TEM images of (c) SWCNT [88] and (d) MWCNT [87]

The atomic structure of a typical SWCNT can be described analogically as a tubular structure, which is formed by ‘rolling’ a graphene sheet into a tube with few-nanometres diameter. The tubular structure of a synthesized CNT often ends with a semi-spherical buckyball fullerene structure for a close-end CNT. The close-end structure is as shown in Figure 2 - 17(d). Attributed to the unique structure, the CNT possesses exceptional electrical, mechanical, and FE properties [89]. In fact, the general properties of CNTs are summarized in Table 2 - 6.

Table 2 - 6: General Properties of CNT [90]

Properties	Values	Comments
Aspect ratio	1000 – 10000	Possibly higher
Tensile strength	> 45 GPa	
Tensile modulus	1 – 1.3 TPa	Outstanding mechanical properties
Flexural modulus	1.2 TPa	
Thermal stability	> 3000°C	In oxygen-free condition
Electrical conductivity	10^4 - 10^7 S/cm	Better than metallic conductor
Electron emission	10^6 - 10^9 A/cm ²	Highest current density reported

As for the electron emission-related applications, the amazing properties of CNTs contribute to the outstanding FE performance. As depicted in Table 2 - 6, CNT has extremely high aspect ratio, which may be as high as 10000. The exceptionally high aspect ratio appears to be a contributing factor to the FE performance of CNT. Additionally, the outstanding mechanical properties of CNT can be attributed to the strong C-C covalent bond atomic structure [91]. The C-C covalent bond atomic structure of CNT hinders back scattering-induced deterioration. Unlike the Spindt-type cathode, the strong covalent bond in CNT can be postulated to be less susceptible to cathode damages due to bombardment of positive ions. At the same time, CNT possesses higher electrical conductivity than most metallic conductors, with its thermal stability at above 3000°C in the absence of oxygen particles. The high electrical conductivity of CNT contributes linearly with its FE density; while the thermal stability of CNT prevents it from thermal-induced damages due to possible localized heating during electron emission.

The electron emission density of a single SWCNT can range from 10^6 - 10^9 A/cm². Due to the high emission current density, CNT offers a promising potential in various FE-related

applications. Nevertheless, the FE density from a continuous CNT film (or CNT array) exhibits lower emission density, when compared to a single SWCNT (as presented in Table 2 - 5). The details of this phenomenon are explained in the next section.

2.5.2 Simulated Field Emission (FE) Characteristics of Carbon Nanotubes (CNTs)

Generally, the FE phenomenon takes place when the energized electrons in the conduction band are tunnelled through the vacuum potential barrier under electrical field [92]. The number of electrons that passes through the vacuum potential barrier is primarily determined by the work function (ϕ) of the surface and the applied electrical field (E), as noted in Fowler-Nordheim's (FN) equation. However, the derivation of FN equation is based on the assumption that the properties of the emitter are similar to those of a sharp metallic tip [93]. As for CNT with semi-spherical or open-ended tips, the FE characteristics may not share identical behaviour with the ideal FN field emitters. Hence, it is important to first identify the primary field emitting region of CNT.

Figure 2 - 18 illustrates the varied CNT shapes and their associated electric field strength at the apex. Amongst the simulated CNT shapes, those with hemispherical cap and cap free shapes best resemble the shape of the actual CNT (open-end and close-end). Besides, it was reported that the highest electrical field strength occurs at the centre of the CNT apex for hemispherical-capped CNT; while the highest electrical field strength takes place along the torus region for capped-free CNT [94]. Moreover, the intense electrical field along the torus region can be explained by the FE mechanism of vertical graphitic walls. As for graphitic walls, it was simulated that the primary emission source is the dangling bonds located at the edges of the wall. These dangling bonds can also be found on the tip of the open-end (capped-free) CNT [95]. Apart from the various shapes of CNT tip, the radius of the CNT also determines the electrical field strength of CNT tips. Figure 2 - 18(b) displays the electrical field strength of

CNT with varying radii. The figure further shows that a CNT with smaller radius accumulates higher electrical field strength at the apex.

Figure 2 - 18: (a) Various CNT shapes; and their associated (b) electric field strength at CNT apex [94]

Due to the tip-emission nature of the FE cathode (cold cathode), the electrical field strength at the CNT tip correlates directly with the emission current, as portrayed in FN equation. Nonetheless, the electrical field of individual CNT tends to neutralize each other in a continuous CNT array. This phenomenon is called ‘screening effect’ [96]. This screening effect is further illustrated in Figure 2 - 19. It shows that a single CNT has more intense electrical field on the tip, while the tips in a CNT array have relatively weaker field strength. Due to the screening effect between CNTs, the FE density of the CNT array decreases with the increasing tube density, as presented in Figure 2 - 20 [97]. This explains the extreme variance in FE density between a single CNT and a continuous CNT array, as elaborated in the previous section. Due to the presence of screening effect in a single CNT, the electric field strength of the apex becomes intense, which further causes the electron emission density to be higher. In

contrast, the electric field of each CNT in an array is reduced by screening effect, thus resulting in less-intense electrical field and lower electron emission density.

Figure 2 - 19: Electrical field (lines) distribution of (a) CNT array, and (b) individual CNT [97]

Figure 2 - 20: Electrical field strength at CNT apex as a function of the average density of CNT for a CNT at a height of $8 \mu\text{m}$ [97]

The simulated results of the CNT showed that CNT array with small CNT radius and low average tube density generated high FE density. The simulated results offer a solid foundation for the fabrication of high emission density CNT array. Due to the promising frontiers of CNT-based cold cathodes, many studies have been reported to optimize the growth of CNTs. The present stage of CNT studies related to FE is further discussed in the following section.

2.5.3 State-of-the-art High Field Emission (FE) Carbon Nanotubes (CNTs)

To date, the most widely used technique for CNTs growth is the Chemical Vapour Deposition (CVD). Due to the low-cost and simple fabrication process, CVD has been widely used commercially for CNT growth. Figure 2 - 21 illustrates the schematic diagram of a typical CVD setup. Prior to the CVD growth process, a catalyst-deposited silicon substrate is usually prepared. The typical catalyst layers used for CNT growth are Nickel (Ni), Iron (Fe) or Cobalt (Co) with thickness ranging from 1 to 20 nm. Additionally, a barrier layer (Aluminium or Titanium) is also deposited on the silicon substrate before catalyst deposition in order to prevent diffusion of catalytic particles into the silicon substrate. Moreover, in a typical CNT synthesis, the catalyst is initially heated to elevated temperature of 600-1000 °C to form catalytic nanoclusters. Next, hydrocarbon gas is introduced into the heated chamber. When the hydrocarbon vapour makes contact with the metal nanoparticles, the gas species decomposes into carbon and hydrogen molecules. The hydrogen gets purged away by the flowing gas, whereas the carbon is dissolved into the metal. At the carbon-metal solubility limit point, the dissolved carbon atoms are precipitated out and crystallized to form a tubular structure [98]. For a more enhanced CNT alignment and lower synthesis temperature, Plasma Enhanced Chemical Vapour Deposition (PECVD) can also be used [99].

Figure 2 - 21: Schematic diagram of a CVD setup [98]

In the attempt to minimize the screening effect among CNTs (as discussed in the previous section), catalyst dots with specified area and inter-dot separation are usually applied to replace the continuous catalyst thin film. As depicted in Figure 2 - 22, individual CNT bundles are grown on photolithography-patterned catalyst dots to minimize mutual neutralization of electrical field on the CNT tips. The preliminary optimal separation distance of individual tube is equivalent to the height of the tube, as proposed by Suh et al., [96]. Nevertheless, the calculation of the optimal distance between individual CNT bundles is more complex. With that, further exploration is demanded to determine the optimal separation distance for more enhanced FE characteristics.

Figure 2 - 22: SEM images of CNT grown on catalyst dots (a) Patterned CNT, and (b) Individual CNT pillar [100]

In utilizing the established CVD technique, many studies have been carried out to optimize the FE characteristics of CNT. For instance, Rao et al., reported a synthesis of Multi-Walled Carbon Nanotubes (MWCNTs) using xylene-ferrocene as the carbon-catalyst source. In this reported technique, the xylene-ferrocene mixture was continuously injected into a preheater so as to vaporize at the temperature of 200 °C. Next, a stream of Argon/Hydrogen gas swept the vapour into the furnace and maintained at 700 °C. The vaporized xylene-ferrocene mixture was then decomposed to form an aligned MWCNT array on the substrate. The resulting FE density ranged from 1 to 3 A/cm² and it was maintained for 2 hours under the applied field of 8-10 V/μm [101]. In fact, a similar method was also reported by Navitski et al., whereby a volatile catalyst source (xylene-ferrocene mixture) was employed to preferentially grow CNT on Silicon wafer. The obtained MWCNT showed a FE density of 3.5 A/cm² under the applied field below 15 V/μm [102].

Apart from altering the hydrocarbon/catalyst sources, another approach that enhanced the FE characteristics of CNT is to enhance the CNT-substrate adhesion. For example, Chen et al., reported the fabrication of CNT with sandwich-structure catalyst layers, as illustrated in Figure 2 - 23. In the sandwich-structure, the thick (150 nm) nickel layer served as a buffer layer to form a NiSi (or Ni₂Si) phase with the silicon substrate for enhanced adhesion. Meanwhile, the Aluminium functioned as a barrier layer to prevent diffusion of iron particles into the nickel layer. The main catalyst source in this structure is the thin (2 nm) iron layer. The corresponding average current density of the grown CNT reached 3.5 A/cm² under the applied field of 5 V/μm, and maintained at 2.5 A/cm² for 2 hours [103].

Figure 2 - 23: Schematic diagram of a sandwich-structure catalyst layers

Besides optimizing the growth conditions and the parameters, post-growth treatment can also be used to enhance the FE characteristics of CNT. As such, Kato et al., reported the annealing and the ‘rooting’ technique of CNT. In the study, CVD-grown Multi-walled CNT was first dispersed in acetone and spin-coated evenly on a titanium foil placed on a tantalum substrate. Next, the substrate was annealed in elevated temperature above 1400 K in a high vacuum condition (10^{-4} Pa) for a prolonged period. As a result, the formation of titanium carbide phase was observed between CNT and titanium coating. In precise, the CNT was ‘rooted’ into the titanium surface via formation of carbide phase [104]. In a separate report, the rooted CNT was aged in Ruthenium Tetroxide (RuO_4) solution for a fixed period of time, ranging from 30 minutes to 24 hours [105]. The formation of Ruthenium (IV) Oxide (RuO_2) particles was observed on the CNT body. The obtained CNT film exhibited an emission current density of 5 A/cm^2 under the applied electrical field of $6 \text{ V/}\mu\text{m}$ for nearly 1000 hours [104].

In enhancing the substrate adhesion of CNTs onto the substrate, a screen-printed CNT paste was reported to deliver high and stable FE current density [106]. For example, Lei et al., reported a fabrication of screen-printed CNT cathode for X-Ray applications. In the reported study, CNTs were mixed with Bi powders, ethyl cellulose, and terpineol to enhance the electrical properties of CNT field emitter, thus attaining high current density of 11.2 A/cm^2 under $12.75 \text{ V/}\mu\text{m}$ applied electric field [107]. Meanwhile, Chen et al., reported an FE current density of 4.5 A/cm^2 under applied field of $10.3 \text{ V/}\mu\text{m}$ by mixing CNTs with terpenol, ethyl cellulose, and Ni powder [108].

Additional to the growth parameters and the post-growth treatments, the operating conditions of a CNT cathode can also affect the resulting FE characteristics. A significant factor to obtain optimal FE density is the effective emission area. As such, Izrael'yants et al., reported the fabrication of small-area (0.01cm^2) CNT array with the conventional CVD method. The emission area was kept small intentionally to diminish anode heating. As the effective emission area shrunk, high emission density was achieved at a relatively smaller emission current. The diminishing anode heating stabilized the transmission of electron by minimizing the heat-induced mechanical deformation of the anode. The fabricated CNT portrayed an emission density of 1.4 A/cm^2 under applied electrical field of $9\text{ V}/\mu\text{m}$ for 100 minutes [109]. The emission characteristics of CNT in the state-of-art are summarized in Table 2 - 7.

Table 2 - 7: Emission Characteristics of CNT in the state-of-art

Fabrication technique/Operating condition		Applied electrical field ($\text{V}/\mu\text{m}$)	Emission density (A/cm^2)	current	Ref.
Xylene/Ferrocene catalyst injection	volatile	8 - 10	1 – 3		[101]
Xylene/Ferrocene catalyst injection	volatile	Below 15	3.5		[102]
Nickel buffer layer		5	3.5		[103]
Rooting and RuO_4 aging		6	5		[104]
Screen-printed CNTs		10.3	4.5		[108]

The amazing CNT FE properties project promising prospects to its application in modern miniaturized TWTAs. Nevertheless, not many studies have extensively looked into the application of CNTs upon TWTA. Therefore, a comprehensive study on the fabrication of CNT field emitter for TWTA application is called for.

Chapter 3: Motivation and Objectives

3.1 Motivation

As discussed in Section 2.1, a continuous increasing trend has been noted in the global satellite industry revenue since the past decade. When compared to year 2007, the global satellite industry revenue doubled in year 2016, hence hitting a whopping amount of \$261 billion. Among the launched satellites, 35% of them are used in commercial communication, indicating the high market potential of commercial communication satellites. In the area of communication satellite, a high Ka-Band has been recently released to relief the congestion among the existing frequency bands. Nonetheless, due to the limited small-sized, wide bandwidth, and high frequency capability amplifying device; the usage of small satellites (1 – 50 kg) in Ka-Band commercial communication is rather limited.

Despite of such continuous advancement in the Solid State Power Amplifiers (SSPA) technology, the use of MVED is still favourable in satellite applications. This can be much attributed to high output power, wide operational frequency, and excellent thermal tolerance of MVED, as depicted in Section 2.2. Among the varied MVEDs, the TWTAs have occupied more than 50% of vacuum electron devices market due to its exceptional signal-amplifying performance. Nonetheless, despite of its high frequency operation, the bulkiness of TWTAs has limited its usage among small satellites.

Furthermore, in the continuous effort of miniaturizing TWTAs, Chua et al., has proposed a microfabricated PH-SWS [110] to substitute the conventional helix slow-wave circuit, as illustrated in Figure 2 - 9. Meanwhile, the proposed PH-SWS is presented in Figure 3 - 1. From the illustration, the PH-SWS is comprised of alternatively-patterned copper bridges and electroplated copper pillars, which can possibly be microfabricated by using Si-based

fabrication techniques. Furthermore, in the attempt to realize the application of PH-SWS in TWTA, the conventional thermionic emitter used in TWTAs is no longer suitable due to its bulkiness and high temperature operation, which can lead to thermal-induced deterioration to its neighbouring microfabricated components. Hence, a miniaturized and high current density field emitter is in need.

Figure 3 - 1: Schematic diagram of PH-SWS [110]

As discussed in Section 2.5, Carbon Nanotubes (CNTs) have been proven to exhibit excellent FE properties due to its exceptionally high aspect ratio. As tabulated in Table 2 - 7, high FE current density in the range of A/cm^2 by CNT field emitter has been reported. Nevertheless, some research gaps that need to be bridged have been identified to realize the application of CNT field emitter in PH-SWS TWTA. Initially, not many studies have looked into the design and the fabrication of CNT field emitter to be used in microfabricated PH-SWS TWTAs. At the same time, only a handful of researches have systematically compared FE properties of CNTs grown by using various techniques, including Plasma-Enhanced Chemical Vapour Deposition (PECVD), floating catalyst Chemical Vapour Deposition (CVD) with ferrocene/xylene source, and pre-deposited CVD using iron catalyst, to name a few. As the

CNT growth technique determines its geometrical and structural properties [111], which exert the direct influence on FE properties of corresponding CNTs [94], the comparative study should offer useful guidelines in fabricating the CNT field emitter for PH-SWS TWTA application. The roadmap of the motivation is summarized in Figure 3 - 2.

Figure 3 - 2: Motivation roadmap for this PhD study

3.2 Objectives

Based on the abovementioned research gaps, the main objective of this PhD thesis is described as follow:

- To design and to fabricate a CNT field emitter that is capable of inducing > 20 dB theoretical signal gain in PH-SWS TWTA under Ka-Band operation, based on the PIC simulation outcomes.

In order to achieve this particular objective, several minor goals need to be achieved, including:

- To determine the electron emission condition required to achieve > 20 dB signal gain in PH-SWS TWTA under Ka-Band frequency.
- To determine the most favourable growth technique of current-emitting CNTs to attain high FE current density.
- To design and to fabricate a CNT field emitter using the selected CNT growth technique for high FE current density.
- To simulate the signal-amplifying performance of PH-SWS TWTA using the obtained FE properties of fabricated CNT field emitter.

Chapter 4: Simulation of Planar Helix-Slow Wave Structure

Traveling Wave Tube Amplifier

Based on Chapter 2, the signal gain in TWTA has been proven to correlate directly with the electron beam current. In this Chapter, the simulation of Particle-In-Cell (PIC) upon PH-SWS TWTA is elaborated so as to determine the requirement of electron beam condition in attaining > 20 dB signal gain. Additionally, the present limitation of PH-SWS TWTA is also listed and weighed in for fabrication of Carbon Nanotube (CNT) field emitter.

4.1 Introduction

As explained in Section 2.2, the electron beam current determines the signal gain of TWTA. Furthermore, Equations (3) and (4) portray that higher electron beam current yields higher signal gain. Hence, in the case of PH-SWS TWTA, the geometrical shape of the SWS differs from the conventional circular helix SWS, and the correlation between electron beam current and signal gain cannot be completely represented by Equations (3) and (4). Hence, in order to determine the electron beam current that is required to attain > 20 dB signal gain in PH-SWS TWTA, Particle-In-Cell (PIC) simulation is needed to determine the signal gain in PH-SWS TWTA.

In this study, the effect of beam current on the signal gain of PH-SWS TWTA is simulated using PIC framework. A few assumptions are made in the simulation. First, the emission of the electron emitter is assumed to be uniform. At the same time, the electron trajectory of the emission is assumed to be perpendicular with the emitter surface. Finally, the initial velocity and the associated kinetic energy of the emitted electrons are assumed to be the same.

4.2 Effect of Electron Beam Current on the Signal Gain of PH-SWS TWTA

The signal gain of PH-SWS TWTA was simulated by using the CST PARTICLE STUDIO SUITE®. Figure 4 - 1 illustrates the schematic diagrams of the PH-SWS TWTA. The dimensions of the components in PH-SWS, as illustrated in Figure 4 - 1(c), are tabulated in Table 4 - 1, similar to the design reported by Zhao et al., [110]. The dimension of the PH-SWS for a single period was fixed at $700 \times 300 \mu\text{m}$ to be operated in Ka-Band [14]. Besides, in order to fit the emitted electron beam into the PH-SWS, the electron emitter for this work was assumed to consist of an effective emitting area of $350 \times 150 \mu\text{m}$ (Figure 4 - 1(b)), which is approximately half of the PH-SWS cross-sectional dimension. Additionally, an accelerating voltage of 5 kV was used, while both the input signal voltage and the frequency had been 10 mV and 30 GHz, respectively. A magnetic field of 0.2 T, parallel to the direction of the electron beam propagation, was applied to confine the electron beam within the PH-SWS. The simulation parameters applied in this study are listed in Table 4 - 2.

Figure 4 - 1: Schematic diagram of: PH-SWS TWTA under (a) and (b) orthogonal view, (c) cross-sectional view, and (d) PH-SWS under orthogonal view

Table 4 - 1: Dimensions of the PH-SWS in Micrometre

h_1	h_2	w_1	w_2	w_3
200	100	300	600	100
VD	E_1	$2a$	$2b$	
100	200	300	700	

(in μm)

Table 4 - 2: Simulation Parameters of PH-SWS TWTA

Parameters	Values
Electron Beam Voltage	5 kV
Input Signal Voltage	10 mV
Input Signal Frequency	30 GHz
Focusing Magnetic Field	0.2 T

In a typical operation of the PH-SWS TWTA, the electron beam is emitted from the electron emitter to drift through the SWS. Due to the inter-electron repulsion, electrons tend to “spread-out” when propagating in a vacuum space. Therefore, an applied magnetic field of 0.2 T (as indicated in Table 4 - 2) is applied to “compressed” to compress the electron beam, in order to fit the beam into the PH-SWS TWT. As such, the input signal inserted into the SWS interacts with the electron to form electron ‘bunches’, where the energy lost from the electron ‘bunching’ is transferred to the PH-SWS for signal amplification [112]. As shown in Figure 4

- 2(a), the lost energy from electron bunching increases gradually along y-axis, agreeing well with the theoretical postulation reported earlier [54], [113], and as illustrated in Figure 2 - 10. The electrons interact with the RF as it enters the PH-SWS region. Since RF behaves as an AC voltage in PH-SWS, electrons accelerated differently in PH-SWS, depending on the instance where a single electron enters the PH-SWS region (crest, trough, or zero point). Since electrons travel in various velocities, electrons with higher velocities will “bunch” with electrons with lower velocities to form bunches. This bunching phenomenon causes electrons to lost energy. As a result, the lost energy from electron bunching is transferred to SWS, hence amplifying the input voltage in SWS signal [53], as illustrated in Figure 4 - 2(b). This signal amplification can also be visualized in Figure 4 - 2(c) and (d), where the electric field on the PH-SWS is amplified with the presence of electron beam.

Figure 4 - 2: (a) Electron ‘bunching’ in TWT; (b) Input and output signals of PH-SWS TWTA operated under 10 mA beam current; electric field distribution on PH-SWS (c) before, and (d) after amplification

In the attempt to investigate the effect of beam current upon the signal gain of PH-SWS TWTA, PIC simulation was performed on TWTA by using varied beam current values from 2 – 40 mA, and the retrieved results are plotted in Figure 4 - 3. The PH-SWS TWTA experienced a continuous increment in the signal gain as the beam current was increased from 2 to 25 mA. After that, the signal gain experienced saturation at 25 mA, and later reduced as the beam current was further increased from 25 to 40 mA. Hence, in order to achieve a signal gain of > 20 dB, the minimum electron beam current of 10 mA was needed from a $150 \times 350 \mu\text{m}$ rectangular emitter. This agrees well with Wang et al., where ~10 mA electron beam current is needed to achieve > 20 dB signal gain [14], [15]. Nevertheless, the simulated signal gain of PH-SWS TWTA at various electron beam current is carried out based on the assumption where the electron beam current is stable, as mentioned in the previous section. In actual operation of PH-SWS TWTA, fluctuation of electron beam current may affect the overall signal gain performance of TWTA, which can be subject to future investigation.

Figure 4 - 3: Signal Gain of PH-SWS TWTA at various beam current values

Apart from signal gain, the possible collision of electron beam onto the PH-SWS of the TWTA was also examined. As the electron beam underwent Brillouin Flow from its interaction

with the focusing magnetic field, the average diameter (a) of the electron beam is expressed as follows:

$$a = \frac{1}{B} \left[\frac{2I}{\pi\eta\varepsilon_0 u_0} \right]^{1/2} \quad (12)$$

Where B , I , η , ε_0 , and u_0 represent magnetic flux density, electron beam current, electron charge to mass ratio, dielectric constant of free space, and beam velocity, respectively [114]. Besides, Equation (12) depicts that the beam diameter does correlate positively with the beam current. In the case of sheet beam, the resulted electron flow displays an elliptical cross-section, as presented in Figure 4 - 4.

Figure 4 - 4: Elliptical cross-section of the electron beam at (a) 10 mA, (b) 20 mA, and (c) 40 mA electron beam current; as well as (d) y-z plane of 40 mA electron beam

Based on Figure 4 - 4, the electron beam expanded as the beam current increased, aligning well with (1). As the beam current hit 20 mA, the electron beam emitted from the electron emitter ($350 \times 150 \mu\text{m}$) expanded to a dimension where it could no longer fit into the PH-SWS ($700 \times 300 \mu\text{m}$), resulting in the collision of electrons onto the PH-SWS (Figure 4 - 4(b)). As the current hiked to 40 mA, the electron beam further expanded, thus resulting in

severe collision of electrons onto the PH-SWS (Figure 4 - 4(c)). This collision caused distortion in signal amplification and damages in PH-SWS. Based on Figure 4 - 4, the signal gain of TWTA declined as the electron beam current exceeded 25 mA due to loss in electron bunching, as the electric field in PH-SWS began failing to keep the electrons in bunches. Lastly, it shows that the electron beam lost its bunches at 40 mA beam current. As compared to Figure 4 - 2(a), no periodical bunching phenomenon is observed in Figure 4 - 4(d). This loss in electron bunching explains the reduction in signal gain as the electron beam current exceeded 20 mA. Thus, the beam current of this proposed PH-SWS TWTA design was kept below 20 mA for optimal functionality.

Additionally, in order to avoid electron collision onto PH-SWS, the rotational tolerance of electron emitter was considered. By slightly tilting the electron emitter, as shown in Figure 4 - 1(b), the degree of rotational tolerance along x - and z -axes were determined, as tabulated in Table 4 - 3. The results of tolerances showed that the electron beam did exhibit lower tolerance at higher beam current. Hence, despite of the higher signal gain from higher electron beam current, a significant drawback for high beam current is the low degree of tolerance, which may be challenging in assembling the electron emitter into PH-SWS TWTA. Therefore, to realize the practical application of PH-SWS TWTA, lower electron beam current of ~10 mA is desirable as it provides higher rotational tolerance in assembling electron emitter with PH-SWS.

Table 4 - 3: Degree of Rotational Tolerance of Field Emitter at Varied Electron Beam Current Values

ELECTRON BEAM CURRENT (mA)	x-axis	z-axis
6	2.6°	1.3°
8	2.2°	1.1°
10	1.7°	1°
14	0.9°	0.4°
18	0.2°	0.3°

4.3 Design and Simulation of Beam-Forming Electrode for PH-SWS TWTA

The results in Figure 4 - 3 show that a minimum electron beam current of 10 mA from 150×350 μm rectangular emitter was needed to gain > 20 dB signal gain in PH-SWS TWTA. This emission condition corresponded to 19 A/cm² emission current density, which may be difficult to achieve from Carbon Nanotubes (CNTs) field emitter. So as to resolve this issue, a field emitter with larger cathode area (~600×1250 μm) was designed for more electron emission (correspondence to higher electron beam current). Besides, the 10 mA electron beam current emitted from the 600×1250 μm cathode area corresponded to ~1.5 A/cm² emission current density, which is significantly lower than 19 A/cm² emitted from 150×350 μm emitter.

Next, a Beam Forming Electrode (BFE) was designed and simulated to ‘compress’ the electron beam to fit into the $300 \times 700 \mu\text{m}$ PH-SWS.

The schematic diagram of the BFE is illustrated in Figure 4 - 5(a), and the details of the BFE-cathode assembly is described in a prior work reported by Wang et al., [15]. Meanwhile, Figure 4 - 5(b) and (c) display the electron trajectory and the electric field distribution in BFE and TWTA. Besides, Figure 4 - 5(b) shows the convergence of electron beam from $600 \times 1250 \mu\text{m}$ to $160 \times 240 \mu\text{m}$. The electron convergence is attributed to the presence of negative field region induced by BFE, as shown in Figure 4 - 5(c). Due to the presence of negative field region, electrons are compressed into a narrow beam with $160 \times 240 \mu\text{m}$ beam waist as indicated in Figure 4 - 5(b). Beyond the beam waist position, the electrons started to spread, as the inter-electron repulsion force reaches a level where the negative field region can no longer further compress the beam. Nevertheless, in actual design of PH-SWS TWTA, the focusing magnetic field will be applied onto the beam at the PH-SWS region, restricting the spread of electron by using the obtained $160 \times 240 \mu\text{m}$ beam waist with 10 mA emission current. This beam waist dimension is significantly smaller than the PH-SWS dimension of $350 \times 700 \mu\text{m}$, where the compressed electron beam could drift through without any electron collision.

Figure 4 - 5: (a) Schematic diagram of BFE, (b) Electron Trajectory, and (c) Electric field distribution in both BFE and TWTA

4.4 Summary

From the abovementioned outcomes, several points are worth highlighting. Signal amplification by TWTA was demonstrated, in which its amplification mechanism was performed through the interaction between RF signal inserted in PH-SWS and electron beam, as illustrated in Figure 4 - 2. Besides, in order to obtain a signal gain of > 20 dB, the electron beam current of 10 mA from $150 \times 350 \mu m$ rectangular emitter had been required. In order to reduce the required current density, an electron emitter with larger cathode area ($600 \times 1250 \mu m$) was designed to obtain more emitted electrons, which corresponded to higher electron

beam current. Next, the electron beam was ‘compressed’ by the BFE into $60 \times 200 \mu\text{m}$ beam waist, which could be fitted into the 300×700 PH-SWS. Hence, an electron emitter that emits $\sim 1.5 \text{ A/cm}^2$ current density from $600 \times 1250 \mu\text{m}$ rectangular cathode area had been required for further analyses.

Figure 4 - 4 presents the electrons hitting the PH-SWS as the beam current reached 20 mA. At the same time, despite of the high signal gain linked to the high beam current, a significant drawback from the high beam current is the stringent rotational tolerance of the electron emitter, as shown in Table 4 - 3. From the simulation results, a comprehensive understanding on the signal gain of PH-SWS TWTA was obtained and thus, taken into account when fabricating CNT field emitter.

4.5 Publications

Y. D. Lim, D. Grapov, X. Xia *et al.* “Design and Fabrication of Carbon Nanotubes Field Emitter for Microfabricated Traveling-Wave Tube,” *IEEE Transactions on Nanotechnology* - Submitted

Y. D. Lim, J.T. Chen, C.B. Yan *et al.* “Hexagonal Mesh Screen-Printed Carbon Nanotubes Field Emitter for Microfabricated Traveling Wave Tube”, *IEEE Transactions on Electron Devices* - Submitted

Chapter 5: Field Emission (FE) Properties of Carbon Nanotubes:

Plasma-Enhanced Chemical Vapour Deposition (PECVD)

Growth Technique

It has been discovered in the previous chapter that an electron emitter capable of emitting ~ 1.5 A/cm² current density from 600×1250 μ m rectangular cathode area to achieve > 20 dB signal gain in PH-SWS TWTA. Therefore, in order to achieve such performance, varied Carbon Nanotubes (CNTs) growth techniques were investigated so as to choose the most viable technique to grow high FE current density CNTs. In this chapter, the FE properties of CNTs grown via PECVD technique, as well as 3D CNT network, are presented.

With that, Section 5.1 elaborates the FE properties of the pristine PECVD-grown CNT films in both as-grown and ethanol-densified conditions. Meanwhile, in Section 5.2, CNTs of smaller diameter were incorporated into the densified PECVD-grown CNTs so as to produce 3D CNT network. The FE properties of the 3D CNT network were further investigated by comparing them with the densified PECVD-grown CNTs.

5.1 As-Grown and Densified PECVD-grown Carbon Nanotube (CNT) films

In this section, the CNTs were grown using the Plasma-Enhanced Chemical Vapour Deposition (PECVD) technique, and the corresponding FE properties were measured. In order to explore further the improvement in FE current density, the PECVD-grown CNT film was densified by using the ethanol evaporation technique to form conical-shaped clusters.

5.1.1 Experimental Method

The CNT was grown via PECVD technique, where 30-nm-thick Ti, 50-nm-thick TiN, and 20-nm-thick Ni, respectively, which served as barrier, adhesion, and catalytic layers, had been

deposited sequentially on n-doped Si substrates (Thickness: 300 μm , Resistivity: 0.018 $\Omega\cdot\text{cm}$).

As for the PECVD process, the Ni catalyst was initially pre-treated with NH_3 gas at 625 $^\circ\text{C}$ for 10 minutes under plasma power (90 W). The growth technique was fine-tuned to obtain a CNT film of approximately 10 – 11 μm height. Subsequently, the CNTs were grown at 750 $^\circ\text{C}$ at NH_3 and C_2H_2 flow rates of 250 and 50 sccm, respectively.

Next, CNTs morphologies were characterized by using both Scanning Electron Microscope (SEM, JEOL JSM-IT100) and Transmission Electron Microscope (TEM, Phillips Tecnai 20). The FE properties of the CNT films were measured by using a planar-anode measurement system under high vacuum condition (10^{-4} Pa). In fact, the measurement was performed by employing a pulsed voltage source. The cathode-anode distance was estimated to be 25 μm , while the circular effective emission area with 2 mm radius was estimated as well in the measurement.

5.1.2 Results and Discussion

Figure 5 - 1(a) and (b) display the SEM images of PECVD-grown CNTs film at various magnification scales. Sparsely-grown, the vertically aligned CNTs of ~ 10.5 μm height were discovered on the Si substrate. The densification of PECVD-grown CNTs is portrayed in Figure 5 - 1(c) – (f), where CNTs formed near-conical shaped clusters after densification. As mentioned in the previous section, ethanol is dripped onto the CNT film and dried naturally. As the ethanol evaporates, the capillary forces between CNTs pulled CNTs together to form clusters [115]–[117]. Since this ethanol densification technique is an established technique to determine the density of CNTs [115], the formation of clusters can be expected to be reproducible. However, there is no study reporting on the accurate control the pitch sizes, such as height and base diameter of the conical shape, pitch of the conical array, etc. To further investigate the morphological properties of the PECVD-grown CNTs, a TEM analysis was performed on the CNTs (Figure 5 - 2). Figure 5 - 2(a) and (b) show the tubular structure of

PECVD-grown CNTs with an outer diameter of ~ 100 nm. Besides, metal cluster was found on the closed CNT tip, as shown in Figure 5 - 2(b). The obtained CNT morphology is similar to the TEM images reported by Baro et al., [118], which justifies the formation of CNTs via PECVD process.

Figure 5 - 1: SEM images of PECVD-grown CNTs: Cross-sectional view of as-grown CNT film at (a) x4000, and (b) x25000 magnification; plane view of (c) as-grown, and (d) densified PECVD film at x1000 magnification; plane view of (e) as-grown, and (f) densified PECVD film at x7000 magnification

Figure 5 - 2: TEM images of PECVD-grown CNTs at (a) lower magnification, and (b) higher magnification

Figure 5 - 3 illustrates the FE characteristics and the Fowler Nordheim (FN) plots of the densified PECVD-grown CNT films. After densification, the PECVD-grown CNT film exhibited ~ thrice increment in FE current density, which escalated from 1.2 to 3.2 mA/cm² under the applied electric field of 8 V/μm. Besides, from the slope of the FN plots, the field enhancement factor (β) of CNT films was calculated by using the FN equation, as described in (9) and (10) [67], [119]. Furthermore, by using the work function value of $\phi = 4.5$ eV [68], the β values of the densified PECVD-grown CNT films were calculated so as to improve from 2732 (as-grown CNT film) to 3214 after densification. The enhancement in β indicated increment in localized electric field on CNT tips [120]. In addition, upon formation of conical-

shaped clusters by CNTs, higher localized electric field on the cluster tips had been speculated, primarily due to CNTs confinement. Such enhancement of electric field is also reported by Chen et al., [121] in a study, where plasma-treated CNTs improved field enhancement due to the formation of tapered-shaped tips [122].

Figure 5 - 3: (a) FE Characteristics, and (b) FN plot of as-grown and densified PECVD-grown CNT films

In further justifying the abovementioned speculation, the electric field distribution in CNT films was simulated via CST STUDIO SUITE®. As such, based on the retrieved SEM and TEM images of the PECVD-grown CNT films (Figure 5 - 1 and Figure 5 - 2), two simplified models were built to approximate the morphological structure of both the as-grown and the densified PECVD-grown CNT films, as illustrated in Figure 5 - 4. In these simplified models, a CNT with the height of 10 μm and 100 nm diameter, along with inter-CNT separation distance of 200 nm, and formation of pyramidal-shaped CNT clusters by 25 CNTs (5x5) after densification, had been assumed. Moreover, external electric field of 10 V/μm was applied on

both models. From the simulation of electric field, the densified CNT films exhibited higher localized electric field on the tips of the clusters, in comparison to the CNT tips discovered in the as-grown CNT film. This is in line with the calculated improvement in β , as well as the associated FE current density of the densified CNT film [123].

Figure 5 - 4: Simulated Electric Field: Orthogonal view of (a) as-grown, and (b) densified CNT film; Cross-sectional view of (c) as-grown, and (d) densified CNT films; (e) localized electric field on the CNT tips

As depicted above, the morphology of the densified PECVD-grown CNTs is similar to that of plasma-treated CNTs reported by Chen et al., [121]. Hence, as suggested, the tapered-shaped CNT tips portrayed enhanced electric field due to plasma ‘trimming’ of CNTs so as to form CNTs with higher aspect ratio. Simultaneously, the reduced diameters of the tapered-shaped CNTs widened the distance of inter-tip, thus resulting in reduced screening effect between the CNTs [121]. Besides, in this study, the geometrical shape and the atomic structure of the CNT itself could be speculated to remain unchanged even after densification [116], [124], [125]. Meanwhile, the electric field enhancement of the densified CNT film could be attributed to the morphological changes that took place in the overall film from continuous and vertically-

aligned CNTs to separated conical-shaped CNT clusters, as shown in Figure 5 - 4. However, both plasma-treated CNTs and liquid-densified CNT film did display enhancement in FE current density via electrical field enhancement, as well as reduction in screening effect.

Based on the FN equation depicted in (9) and (10), the FE current density of an emitter exemplified increment in an exponential manner with its corresponding field enhancement factor (β). In the case of CNT field emitter, the β value was found to increase with higher CNT aspect ratio, or smaller CNT diameter. Thus, in order to further improve the FE current density in PECVD-grown CNTs, one possible way is to incorporate CNTs with smaller diameters, so as to form a three-dimensional (3D) CNT network. The FE properties of this 3D CNT network are discussed in the following section.

5.2 Three-Dimensional Carbon Nanotube (3D CNT) Network

Section 5.1 has revealed that the PECVD-grown CNTs exhibited limited FE current density of 3.2 mA/cm² even after densification. Hence, in order to further explore the enhancement in FE current density, CNTs with smaller diameters were incorporated into the PECVD-grown CNTs, which formed 3D CNT network. This CNT network, which was comprised of thermal CVD-grown CNTs (known as ‘Secondary CNTs’), was found attached onto the bodies of PECVD-grown CNTs (known as ‘Primary CNTs’). With that, this section looked into the FE properties of the 3D CNT network.

5.2.1 Experimental Method

The synthesis process of the 3D CNT network is illustrated in Figure 5 - 5. In preparing all the CNT samples for this study, n-doped Si substrates (Thickness: 300 μ m, Resistivity: 0.018 Ω .cm) were utilised. As presented in Figure 5 - 5, primary CNTs were grown via PECVD process, as described in Section 5.1.1. Next, in the attempt to incorporate secondary CNTs, the primary CNTs were first impregnated with Ni(NO₃)₂.6H₂O in acetone (0.01 mol/L) to decorate

the Ni catalytic particles onto primary CNTs. After that, the secondary CNTs were grown by using the Thermal Chemical Vapour Deposition (TCVD) technique, where the Ni-decorated primary CNTs were heated up to 700 °C under 100 sccm Ar gas flow. At 700 °C, 50 sccm H₂ gas was introduced. By switching the gas flows (Ar and H₂) using an ethanol bubbler, ethanol was added to the gas flow and thus, gave carbon source for the growth of secondary CNT, which was carried out in 700 °C for 10 minutes.

Figure 5 - 5: Synthesis process of the 3D CNT network

Next, so as to rule out the possible impact of Ni(NO₃)₂.6H₂O impregnation upon the FE properties of primary CNTs, the FE properties of Ni(NO₃)₂.6H₂O impregnated primary CNTs were examined, terming the resultants as ‘densified primary CNTs’. At the same time, the FE properties of the pristine secondary CNTs were also investigated. The pristine secondary CNTs were grown by adding some drops of acetone-based Ni(NO₃)₂.6H₂O solution onto 30 nm Ti/50 nm TiN-deposited Si substrate, and followed by the TCVD process described above. Further sample labelling and descriptions are given in Table 5 - 1.

Table 5 - 1: Sample Labelling of 3D CNT network

Sample Labelling	Description
Secondary CNTs	CNTs were grown via TCVD by adding $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ drops on 30 nm Ti/50 nm TiN-deposited Si substrate
As-grown Primary CNTs	PECVD-grown CNTs
Densified Primary CNTs	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ impregnated CNTs
3D CNT network	Secondary CNTs grown on densified primary CNTs

5.2.2 Results and Discussion

The SEM images of both primary and secondary CNTs are presented in Figure 5 - 6. Based on Figure 5 - 6(a), the secondary CNT film exhibited limited thickness of $> 2 \mu\text{m}$ due to the non-vertical growth orientation, as discussed earlier [126]. Besides, the randomized growth orientation discovered among the CNTs could be attributed to the formation of inhomogeneous Ni particles at 700°C , thus resulting in lower Van der Waals force between the CNTs [127]. The formation of inhomogeneous Ni particles is portrayed in Figure 5 - 6(b), which displays CNTs with non-uniform diameters. This is in agreement with the mechanism suggested by Ramirez et al., [128], where the random growth orientation of CNTs is due to the formation of large and inhomogeneous catalyst particles during the TCVD process, hence resulting in randomly-oriented CNTs with non-uniform diameters. In contrast to secondary CNTs, primary CNTs exhibited somewhat higher degree of vertical alignment, as shown in Figure 5 - 6(c) and (d). From Figure 5 - 6(c), the heights of primary CNTs could be estimated to be $\sim 10 \mu\text{m}$, which is similar to the outcome reported in Section 5.1. Besides, the vertical alignment of primary

CNTs could result from the plasma-induced alignment during PECVD growth [99], [129] as suggested by Bower et al., [130].

Figure 5 - 6: SEM images of: Secondary CNTs under (a) cross-sectional, and (b) plane view; primary CNTs under (c) cross-sectional, and (d) tilted view.

It was discovered that primary CNTs formed conical and densified tips upon impregnation by acetone-based $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The densification of primary CNTs took place through the capillary force that occurred between the CNTs during solution evaporation (Figure 5 - 7(a)), as discussed in Section 5.1 [124]. Such densification phenomenon is reflected on the SEM images of 3D CNT network. The densification of primary CNTs could be due to the evaporation of acetone-based solution impregnated upon primary CNTs at 700 °C. From Figure 5 - 7(b) and (c), it can be observed that the 3D CNT network comprises of random-growth CNTs growing on the bodies of vertically aligned CNTs. Since it has been obtained from Figure 5 - 6 that primary CNTs are vertically aligned (Figure 5 - 6(c) and (d)) whereas secondary CNTs are grown in random orientation (Figure 5 - 6(c) and (d)), primary CNTs and secondary CNTs can be identified in Figure 5 - 7(b) and (c).

Figure 5 - 7: SEM images of: (a) densified CNTs; 3D CNTs under (b) plane view, and (c) cross-sectional view

In further investigating the morphological properties of 3D CNTs, several TEM images are presented in Figure 5 - 8. As such, Figure 5 - 8(a) and (b) present the TEM images of PECVD-grown primary CNTs, in which the primary CNTs exhibited multi-walled structure, similar to the CNT structure obtained by Baro et al., [118]. At the same time, the catalyst cluster was found embedded on the tip of the nanotube, hence suggesting the tip-growth mechanism of CNTs [131]. Furthermore, the diameter of the primary CNTs could be estimated to be ~100 nm. The presence of additional secondary CNTs after the TCVD growth of CNTs can be noted

in Figure 5 - 8(c) and (d). From Figure 5 - 6 and Figure 5 - 7, it can be observed that secondary CNTs have significantly smaller diameter as compared to primary CNTs. From this morphological observation, primary and secondary CNTs can be accurately identified under TEM images, as shown in Figure 5 - 8(d) to (f). As portrayed in Figure 5 - 8(d), secondary CNTs were found attached on primary CNTs. This is in line with the speculation discussed in the earlier sections, where secondary CNTs were grown from the Ni particles attached on primary CNTs by $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ impregnation.

Figure 5 - 8: TEM images of: (a) & (b) primary CNTs, (c) & (d) 3D CNTs, (e) & (f): primary-secondary CNTs interface

In order to further justify the growth of secondary CNTs from the primary CNT body, high resolution TEM images were taken at the interface between primary-secondary CNTs, as illustrated in Figure 5 - 8(e) and (f). From Figure 5 - 8(f), the diameter of the secondary CNTs is estimated to be 20 – 22 nm, similar to the diameter measured in a prior study [132].

Meanwhile, the secondary CNTs exhibited multi-walled structure, which is similar to that of the primary CNTs. From the primary-secondary CNT interface, it was noted that the multi-walled structure of secondary CNTs appeared to be extended from the Ni particle attached on the primary CNT, hence indicating the base-growth mechanism of secondary CNTs [133]. Upon combining the abovementioned observations, it can be preliminarily concluded that secondary CNTs were grown from the Ni particles attached on primary CNTs via TCVD process, where the particles were found to be decorated from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ impregnation.

Figure 5 - 9: (a) FE measurements, (b) FN plots of secondary CNTs, as-grown primary CNTs, densified primary CNTs, and 3D CNTs

Figure 5 - 9 presents the FE properties of CNT samples examined in this study. The randomly-oriented CNTs displayed low FE current density of 0.52 mA/cm² under 6.5 V/μm applied field, which further burnt-off as the applied field was increased. This could be attributed to the uneven distribution of localized electric field among the CNTs [134]. Hence,

so as to rule out the possible FE enhancement by densified primary CNTs, the FE properties of the densified CNTs after $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ impregnation were also determined. As projected in Figure 5 - 9(a), under $8 \text{ V}/\mu\text{m}$ applied field, the densified primary CNTs displayed higher FE current density of $3.35 \text{ mA}/\text{cm}^2$ than that of as-grown primary CNTs ($1.32 \text{ mA}/\text{cm}^2$), which appears similar to the ethanol-densified PECVD-grown CNTs reported in Section 5.1. Such enhancement took place due to the improved field enhancement by conical-shaped densified CNTs [135]. When compared to densified primary CNTs, the 3D CNTs exhibited further improvement in FE current density, hence attaining $5.45 \text{ mA}/\text{cm}^2$ under $8 \text{ V}/\mu\text{m}$ applied field. This improved FE current density could be attributed to the field enhancement of secondary CNTs that grew on vertically-aligned primary CNTs, as claimed by Liu et al., [136]. Furthermore, it is also possible that growing secondary CNTs offers more emission sites on primary CNT tips, thus resulting in higher FE current density, as shown in Figure 5 - 7(c).

Meanwhile, the field enhancement factor (β) values of the CNT samples had been determined from their respective FN plots, as presented in Figure 5 - 9(b). As depicted in Figure 5 - 9(b), all the investigated CNT samples displayed near-linear FN plots, which justifies the FN theory in obtaining β values [137], [138]. By using the theoretical CNT work function value of 4.5 eV [139], the β values of secondary CNTs, as-grown primary CNTs, densified primary CNTs, and 3D CNTs were calculated. The β values and the maximum FE current density of each investigated sample are tabulated in Table 5 - 2. As a result, the higher β value of primary CNTs, especially after densification, showed that the vertically-aligned CNTs emitted higher FE current density upon densification due to field enhancement on confined CNT cones [124], [135], which is in line with a prior study [140]. From the retrieved β values and FE current density of the densified primary CNTs and 3D CNT network, the achievement of higher FE current density by 3D CNTs than the densified primary CNTs could be attributed to the additional emission sites offered by the secondary CNTs.

Table 5 - 2: FE properties of primary, secondary, and 3D CNTs

Sample	Current density @ Applied	Field Enhancement
	Electric Field	Factor (β)
Secondary CNTs	0.52 mA/cm ² @ 6.5 V/ μ m	3227.7
As-grown Primary CNTs	1.32 mA/cm ² @ 8 V/ μ m	3421.3
Densified Primary CNTs	3.35 mA/cm ² @ 8 V/ μ m	4343.9
3D CNT Network	5.45 mA/cm ² @ 8 V/ μ m	7067.1

Another possible factor contributing to FE properties of CNTs is the vacuum level. The 10^{-4} Pa chamber pressure used in this study is not the most idealized pressure. As lower chamber pressure gives lower work function to the field emitter, which yields higher FE current density [141]. For instance, high current density with several hundreds of A/cm² is reported under 10^{-9} Pa vacuum level [142]. Nevertheless, the objective of studies carried out in Chapter 5 and 6 is to perform a comparative study between CNTs grown using various techniques (PECVD, pre-deposited catalyst TCVD, and floating catalyst TCVD). Thus, the main concern in Chapter 5 to 6 is to standardize the vacuum level rather than to optimize it.

5.3 Summary

In summary, CNTs grown via PECVD technique exhibited a higher degree of vertical alignment, whereby the CNT diameter was ~ 100 nm. By densifying the PECVD-grown CNTs, its FE current density enhanced from 1.32 to 3.35 mA/cm² under 8 V/ μ m applied field. Hence, so as to further enhance its FE current density, secondary CNTs were grown on primary CNTs to form a 3D CNT network, which resulted in 5.45 mA/cm² FE current density under 8 V/ μ m applied field. Such enhancement in FE properties among the PECVD-grown CNTs could be

attributed to the additional emission sites by secondary CNTs. At the same time, it is also possible that the smaller (20 – 22 nm) diameter of secondary CNTs to yield higher aspect ratio, which enhances the overall β value of CNT network. Therefore, in the attempt to justify this postulation, CNTs of smaller diameter were grown via TCVD technique, as depicted in Chapter 6.

5.4 Publications

Y.D. Lim, Q. Kong, S. Wang *et al.* “Enhanced field emission properties of carbon nanotube films using densification technique”, *Applied Surface Science* – **In Press – Corrected Proof**

Y.D. Lim, Q. Kong, C.W. Tan *et al.* “Field Emission Properties of Three-Dimensional Carbon Nanotubes Network”, *Materials Research Express* – **First Revision Submitted**

Chapter 6: Field Emission (FE) Properties of Carbon Nanotubes (CNTs): Thermal Chemical Vapour Deposition (TCVD) Growth Technique

From the previous chapter, a field emission (FE) current density of 5.45 mA/cm^2 was obtained from 3D Carbon Nanotube (CNT) network. From the FE studies, it has been postulated that the incorporation of CNTs with smaller diameter into PECVD-grown CNTs enhances the overall FE current density.

In this chapter, the FE properties of CNTs with smaller diameters grown via Thermal Chemical Vapour Deposition (TCVD) technique are determined. In Section 6.1, FE properties of the TCVD-grown CNTs using pre-deposited catalyst are presented. Next, so as to explore further improvement in FE current density, Section 6.2 compares the FE properties of TCVD-grown CNTs using between pre-deposited catalyst and floating catalyst.

6.1 Pre-Deposited Catalyst TCVD-grown Carbon Nanotube (CNT) films

In this section, CNTs were grown by using the pre-deposited catalyst TCVD technique, and the corresponding FE properties were measured. From the previous chapter, it has been shown that growing secondary CNTs of smaller diameter improves the FE properties of PECVD-grown CNTs. This improvement can be attributed to the additional emitting sites provided by the secondary CNTs grown by TCVD technique. Besides, the smaller diameter of secondary CNTs grown by TCVD technique yields better field enhancement on CNT tips, resulting in high FE properties [138], [143]. Therefore, to further explore the possibilities in achieving higher FE current density by CNTs, CNT films with smaller CNT diameters (higher CNT aspect ratio) are grown using TCVD technique. Besides, in order to explore further enhancement in FE current density, the TCVD-grown CNT film was densified by employing

the ethanol evaporation technique to form isolated clusters, similar to the densification technique on PECVD-grown CNTs reported in the previous chapter.

6.1.1 Experimental Method

A combination of 8-nm-thick Al, 2-nm-thick Al₂O₃, and 1-nm-thick Fe were pre-deposited sequentially on n-doped Si substrates (Thickness: 300 μm , Resistivity: 0.018 $\Omega\cdot\text{cm}$). As for the TCVD process, the Fe catalyst was initially pre-treated with H₂ gas at 700 °C for 3 minutes, and followed by growth of CNTs at 700 °C with H₂ and C₂H₂ flow rates at 700 and 200 sccm. The growth durations of 1, 2, 3, 4, and 5 minutes were performed for TCVD processes. As for the densification process, the as-grown CNT films, as mentioned above, had been dripped with ethanol (99%) and dried in ambient.

Furthermore, the morphological and the FE characterization conditions are similar to the details described in Section 5.1.1. As for this section, the Raman characteristics of the CNTs were characterized by using WITec Raman system with 532 nm excitation laser source.

6.1.2 Results and Discussion

Figure 6 - 1 illustrates the SEM images of the pre-deposited catalyst TCVD-grown CNTs. The image clearly projects that the CNTs had been indeed densely-packed, vertically aligned, and possessed a height of $\sim 11 \mu\text{m}$. The densification of the pre-deposited catalyst TCVD-grown CNT film is shown in Figure 6 - 1(b) and (c) under similar SEM magnification ($\times 500$). Meanwhile, the magnified view of an individual CNT cluster formed by multiple CNTs is portrayed in Figure 6 - 1(d). The obtained randomized densified pattern of pre-deposited TCVD-grown CNTs, eventually, appears to be similar to that reported by Zhong et al., [144]. Nonetheless, the randomized pattern formed by the densifying pre-deposited catalyst TCVD-grown CNTs differed from the conical-shaped clusters formed in PECVD-grown CNTs (Figure 5 - 1). This could be attributed to the variance in CNT morphologies, where the pre-

deposited catalyst TCVD-grown CNTs had been densely-packed, while the PECVD-grown CNTs were sparsely-grown. Apart from density, another possible factor for this variation in densification pattern is the CNT diameter.

By comparing Figure 5 - 1 with Figure 6 - 1, the pre-deposited catalyst TCVD-grown CNTs display smaller diameter, in comparison to PECVD-grown CNTs. The smaller diameter (higher aspect ratio) of the pre-deposited TCVD-grown CNTs could have led to lower CNT hardness [145], where CNTs failed in standing alone all due to low rigidity. This is further explained by comparing the mechanisms of alignment for both pre-deposited TCVD- and PECVD-grown CNTs. The alignment of pre-deposited catalyst TCVD CNTs reflected the ‘crowding effect’ [99], where the Van der Waals force between the CNTs offered mutual mechanical support for CNT alignment. On the other hand, the PECVD-grown CNTs could be speculated to possess sufficient rigidity to stand alone, without depending on the ‘crowding effect’. This is proven in Figure 5 - 1, where the PECVD-grown CNTs exhibited vertical alignment even under sparsely-grown condition. As a result, upon densification, the PECVD CNTs generated conical-shaped clusters, while the pre-deposited catalyst TCVD-grown CNTs clusters resulted in random shapes. So as to further investigate the morphological properties of the pre-deposited catalyst TCVD-grown CNTs, TEM analysis was performed on the CNTs (Figure 6 - 2). As illustrated in Figure 6 - 2, the pre-deposited catalyst TCVD-grown CNTs had multi-walled structure with ~47 nm tube diameter. This diameter noted among the pre-deposited catalyst TCVD-grown CNTs had been significantly smaller than that of PECVD-grown CNTs (~100 nm), hence yielding higher CNT aspect ratio, which could possibly lead to higher FE current density [74], [139].

Figure 6 - 1: SEM images of pre-deposited catalyst TCVD-grown CNTs: (a) Cross-sectional view of CNT film; plane view of (b) as-grown, and (c) densified CNT film at $\times 500$ magnification; (d) Individual CNT cluster

Figure 6 - 2: TEM images of pre-deposited catalyst TCVD-grown CNTs: (a) Closed-ended CNT tip, (b) CNTs showing tube diameter of ~ 47 nm

Figure 6 - 3 displays the FE characteristics and the FN plots of pre-deposited catalyst TCVD-grown and PECVD-grown CNT films. Generally, the TCVD-grown CNTs showed ~twice higher FE current density than that of PECVD-grown CNTs. After densification, the pre-deposited catalyst TCVD-grown CNT film exhibited ~ 4 times improvement in FE current density. Meanwhile, the β values of the densified TCVD-grown CNT film displayed improvement from 2851 (as-grown CNT film) to 13660. Such great improvement in β could be attributed to the drastic reduction of CNT coverage area after densification (low filling factor [115]), as presented in Figure 6 - 1(b) and (c). At the same time, the higher FE current density of pre-deposited catalyst TCVD-grown CNT films, in comparison to PECVD-grown CNT films, could be attributed to the higher CNT aspect ratio [146]. Under similar 10 – 11 μm heights of PECVD-grown and pre-deposited catalyst TCVD-grown CNTs, the CNT aspect ratios of both TCVD-grown and PECVD-grown CNTs were 234 and 105, respectively. As such, the higher aspect ratio of the pre-deposited catalyst TCVD-grown CNTs partially justifies the achievement of higher FE current density, especially when compared to PECVD-grown CNTs. Nevertheless, the FE properties of CNTs depend on many other factors (CNT density [147], graphitization of CNTs [148], etc.). It has been reported that the area density of CNTs can significantly affect the FE properties of a CNT film [149], [150]. Therefore, when comparing the FE properties of TCVD- and PECVD-grown CNTs, the difference in CNT density could be one of the contributing factors in the variation in their respective FE performance. However, since TCVD-grown CNTs are generally dense, with relatively smaller diameter; whereas PECVD-grown CNTs are generally sparse, with relatively larger diameter. It is challenging to grow CNTs of similar diameters using both TCVD and PECVD techniques. Therefore, the factor of the area density of CNTs is not “singled-out” when comparing the FE performance of TCVD- and PECVD-grown CNTs in this study. Therefore, the comparison

between TCVD- and PECVD-grown CNTs is only carried out under similar CNT I_d/I_g ratio, CNT heights, and vertically-aligned morphology.

Figure 6 - 3: (a) FE Characteristics, and (b) FN plot of pre-deposited catalyst TCVD-grown and PECVD-grown CNT films

In the attempt to explore the possibility of achieving higher FE current density by CNTs with higher aspect ratio [91], the CNT growth duration in TCVD process was increased to obtain CNT films with varied heights. The CNT growth duration and its associated CNT height are tabulated in Table 6 - 1. Next, the FE properties of pre-deposited catalyst TCVD-grown CNT films are illustrated in Figure 6 - 4. As a result, a maximum FE current density of ~ 3 mA/cm² was retrieved from as-grown CNTs with an aspect ratio of 3-minute growth duration. Upon densification, the pre-deposited catalyst TCVD-grown CNTs exhibited 2 – 4 times enhancement in FE current density after densification. As for the CNTs with 3-minute growth duration, the FE current density increased from ~ 3 to ~ 10 mA/cm² upon densification. Such improvement can be deduced as the enhancement of FE properties in the densified CNT films, hence attributing to the increase in the localized electric field on CNT tips. This field enhancement in pre-deposited catalyst TCVD-grown CNT films is similar to that described in Figure 5 - 4. Apart from the enhancement in FE current density, Figure 6 - 4(b) shows that the

current density of CNT films did not increase continuously with the increasing CNT growth duration, which correlated with their respective CNT aspect ratio. Meanwhile, the pre-deposited catalyst TCVD-grown CNT films displayed maximum FE current density for the 3-minute CNT growth duration (16.7 μm), but a reduction as the growth duration exceeded 3 minutes. Preliminarily, this reduction could be postulated as the shift in structural properties with the increasing CNT length that affected its corresponding FE properties.

Table 6 - 1: CNT height at various growth duration

CNT growth duration (min)	CNT height (μm)
1	11
2	14.3
3	16.7
4	18
5	20.6

Figure 6 - 4: (a) FE Measurements, and (b) FE current density at $7 \text{ V}/\mu\text{m}$ applied field for as-grown/densified TCVD-grown CNT film

In order to further justify the abovementioned postulation, Raman Spectroscopy was performed on TCVD-grown CNTs with heights ranging from 11 to 20.6 μm (1 – 5 min growth durations). From the Raman Spectrum of the CNT films (Figure 6 - 5), it was found that the I_d/I_g ratio of CNT increased with the increasing CNT aspect ratio (or CNT height). Moreover, it has been well-reported that higher I_d/I_g ratio reflects poor CNT graphitization, which could probably reduce its FE current density [148], [151]. Consequently, tall CNTs exhibit higher defectiveness, which leads to higher I_d/I_g ratio obtained. In conjunction with the obtained Raman spectrum of pre-deposited catalyst TCVD-grown CNTs, perhaps the low CNT graphitization factor ended up dominating the FE properties of CNTs with its height increment exceeding 16.7 μm (3-min growth duration), hence resulting in reduced FE current density.

Figure 6 - 5: (a) Raman Spectra, and (b) FE Current Density and I_d/I_g ratio, of TCVD-grown CNTs at different CNT aspect ratios

6.2 Floating Catalyst TCVD-grown Carbon Nanotube (CNT) films

Section 6.1 projects that the pre-deposited catalyst TCVD-grown CNTs exhibited higher FE current density than the PECVD-grown CNTs due to its higher CNT aspect ratio (smaller CNT diameter), which further yielded higher field enhancement on the CNT tips. Nonetheless, as for the pre-deposited catalyst TCVD growth technique, although taller CNTs

resulted in higher CNT aspect ratio, the Raman properties of CNTs were traded-off, thus resulting in inferior FE properties as the height of CNT exceeded 16.7 μm . With that, this section presents the floating catalyst TCVD growth technique carried out to increase the field enhancement on CNT tip without trading off its Raman properties.

6.2.1 Experimental Method

Several CNT films were grown by applying the pre-deposited catalyst and the floating catalyst TCVD techniques. As for the pre-deposited catalyst-grown CNTs, growth durations of 1 and 3 minutes had been selected, where the details of the TCVD process and the catalyst preparation are described in Section 6.1.1. As for the CVD technique using floating catalyst source, bare Si substrate was initially inserted into the reactor. Next, continuous injection of ferrocene/xylene solution (1 wt%) was performed into the reactor at 820 °C under continuous Argon gas flow. For comparison purposes, the growth durations were fine-tuned to grow CNTs of ~11 and ~16 μm in height, respectively.

The morphological, the structural (Raman), and the FE characterization conditions are similar to the details described in Sections 5.1.1 and 6.1.1.

6.2.2 Results and Discussion

Figure 6 - 6 illustrates the SEM images of both pre-deposited and floating catalyst-grown CNT films. From these images, one can clearly observe that CNTs grown by both catalyst sources displayed high degree of vertical alignment, which is in agreement with prior studies that reported on CNT growth using pre-deposited [152] and floating [127] catalyst sources. In fact, the vertical alignment of the pre-deposited catalyst-grown CNTs could be attributed to the ‘crowding effect’ between the CNTs [144], as mentioned earlier. Besides, as asserted by Neupane et al., the degree of vertical alignment is a significant factor in determining the FE properties of CNTs [153]. Hence, in order to facilitate the FE comparison between pre-

deposited and floating catalyst-grown CNTs, vertically aligned CNTs were grown by using both catalyst sources. From Figure 6 - 6, slight significant difference in the degree of vertical alignment between (b) and (d), where (b) appears to be more neatly-aligned than (d). This suggests that floating catalyst-grown CNTs may exhibit inferior vertical alignment as compared to pre-deposited catalyst-grown CNTs, which can be a major factor in influencing the corresponding FE properties [126], [154]. At the same time, Bocharov et al., have reported that the FE properties of CNTs significantly depend on its aspect ratio (height/diameter) due to its directly influence upon field enhancement on CNT tips [155]. Moreover, so as to rule out the possible influence on FE properties by the varying CNT heights, CNTs of similar heights ($\sim 11\ \mu\text{m}$, as displayed in Figure 6 - 6(a) and (c); $\sim 16\ \mu\text{m}$, as shown in Figure 6 - 6(b) and (d)) were grown with pre-deposited and floating catalyst sources, respectively.

Figure 6 - 6: SEM images of (a - b) pre-deposited catalyst, and (c - d) floating catalyst-grown CNTs of ~ 11 and $\sim 16\ \mu\text{m}$ heights

Apart from the CNT height, the structural properties (Raman characteristics) of CNTs have been reported to play a significant role in its FE properties [148]. This could be attributed to the direct correlation between CNT's I_d/I_g ratio and its electrical properties, which has

influence upon its corresponding FE behaviour [151]. Besides, the impact of CNT I_d/I_g ratio upon its corresponding FE current density has also been demonstrated and discussed in Section 6.1. Thus, in ruling out the possible influence by the variance in the structural properties, the growth parameters were fine-tuned in order to gain CNTs with similar I_d/I_g ratio. The Raman Spectra of both pre-deposited and floating catalyst-grown CNTs are presented in Figure 6 - 7. The emergence of D-band ($1339 - 1444 \text{ cm}^{-1}$) and G-band ($1575 - 1577 \text{ cm}^{-1}$) in the Raman spectra for both pre-deposited and floating catalyst-grown CNTs reflected the presence of disorder in the graphitic structure, as well as the in-plane vibration of C-C bond [156]. Hence, by applying the curve fitting technique, as proposed by Ferrari et al., [157], the I_d/I_g ratios of both pre-deposited and floating catalyst-grown CNTs ($\sim 11 \text{ }\mu\text{m}$) were calculated as 0.67 and 0.68, respectively. Besides, Mathur et al., have reported that CNTs do exhibit minimal changes in their electrical properties as the I_d/I_g ratio varies by ~ 0.03 [158]. In comparison to that reported by Mathur et al., the slight variation (~ 0.01) in I_d/I_g obtained in this study could be speculated to exert minimal impact on the electrical properties, as well as the associated FE features. Nevertheless, the electrical properties of CNTs may give significant influence on its corresponding FE properties [159], which require further investigations.

Figure 6 - 7: Raman spectra of both pre-deposited and floating catalyst-grown CNTs

Figure 6 - 8(a) presents the FE measurements of both pre-deposited and floating catalyst-grown CNTs with ~ 11 and ~ 16 μm heights. By using the widely accepted Fowler-Nordheim (FN) equation, the FN plots of the respective CNTs were plotted [68], as portrayed in Figure 6 - 8(b). Additionally, the FE current density and the field enhancement factors of the respective CNTs are tabulated in Table 6 - 2.

Figure 6 - 8: (a) FE measurements, and (b) FN plots of both pre-deposited and floating catalyst-grown CNTs (~ 11 and ~ 16 μm height)

Table 6 - 2: Highest FE Current Density achieved and Field Enhancement Factors of both Pre-deposited catalyst and Floating Catalyst-grown CNTs

Catalyst Sources	CNT Heights	Highest Current Density achieved @ Electric Field (mA/cm² @ V/μm)	β
Pre-deposited Catalyst	~ 11 μm	1.17 @ 7	311
	~ 16 μm	3.02 @ 7	949
Floating Catalyst	~ 11 μm	1.43 @ 6.8	340
	~ 16 μm	3.13 @ 5.3	1060

Table 6 - 2 shows that CNTs exhibited higher FE current density and β values at $\sim 16 \mu\text{m}$ height, in comparison to $\sim 11 \mu\text{m}$ height. This could be attributed to the higher aspect ratio of taller CNTs, hence resulting in higher field enhancement at the CNT tips [160]. Interestingly, at similar heights, the floating catalyst-grown CNTs displayed higher FE current density and β values. Moreover, as the Raman factor of the CNTs has been ruled out (as discussed earlier), a possible factor in influencing the FE properties of CNTs grown from these two catalyst sources would be the morphological shape of the CNTs. So as to further investigate this scenario, a Transmission Electron Microscopy (TEM) study was performed for catalyst-grown CNTs, as shown in Figure 6 - 9.

Figure 6 - 9: TEM images of floating catalyst-grown CNTs

The obtained TEM images illustrate that the floating catalyst-grown CNTs (Figure 6 - 9(a) and (b)) possessed smaller diameters (14 ~ 18 nm), in comparison to CNTs grown from pre-deposited catalyst (Figure 6 - 2(a) and (b)) ($\sim 47 \text{ nm}$). At similar heights of ~ 11 and $\sim 16 \mu\text{m}$, smaller diameters of floating catalyst-grown CNTs yielded higher aspect ratio, when compared to pre-deposited catalyst-grown CNTs. Besides, as depicted in Fowler Nordheim (FN) theory, higher aspect ratio results in higher field enhancement at the CNT tips, thus resulting in higher FE current density [92], [155]. Besides, Figure 6 - 9 exhibits that catalyst clusters were formed at the CNT tips as a result of the grown from pre-deposited and floating

catalyst sources [161]. Interestingly, enlarged tips can be observed on CNTs grown from floating catalyst, but not for pre-deposited catalyst-grown CNTs. This could be attributed to the growth mechanisms for both catalyst sources, as projected in Figure 6 - 10. As for the pre-deposited catalyst, the carbon particles were diffused into the de-wetted catalyst clusters, hence forming a carbon tubular structure when the clusters were saturated with carbon particles [98]. On the other hand, as for the floating catalyst, the iron content from the ferrocene precursor functioned as the catalyst source that fed continuously throughout the whole CNT growth process [162], [163]. Due to such continuous feeding, several enlarged CNT clusters with random shapes were formed, as displayed in Figure 6 - 9(a) and (b).

Figure 6 - 10: CNT growth mechanisms of (a) pre-deposited, and (b) floating catalyst-grown CNTs

In order to investigate the field enhancement effect of enlarged tips, two simplified models of enlarged CNT tips were built to approximate the conical- and spherical-shaped CNT tips, as presented in Figure 6 - 11. In fact, Figure 6 - 11(b) and (d) display that CNTs possessed higher field enhancement on enlarged tips. As for the conical-shaped CNT tip, as shown in Figure 6 - 11(a) and (b), the localized electric field on the tip exhibited increment by ~20% as

the base diameter of the conical shape doubled. This could be attributed to the increase of θ value from $\theta = \sim 45^\circ$ to $\theta' = \sim 54^\circ$, thus resulting in further confinement of electric field at the tip of the cone. Moreover, the increment in field enhancement due to increased θ is similar to the simulation outcomes reported by Goncharenko et al., [164], [165].

On the other hand, similar electric field enhancement on CNT tip was also observed on enlarged spherical tip. Based on Figure 6 - 11(c) and (d), the electric field was ‘confined’ on the spherical tip upon enlargement. This is explained by approximating a fractional part of the spherical tip as the cone tip, as shown in Figure 6 - 11(c) and (d). In fact, similar enhancement of electric field can be anticipated upon enlargement of spherical tip due to the increasing ‘cone angle’ (θ). Nonetheless, since enlarged CNT tips exhibited random shapes, as shown in Figure 6 - 9, the models presented in Figure 6 - 11 do not completely represent the exact field enhancement phenomenon in both pre-deposited and floating catalyst-grown CNTs. However, from the simulated electric field, it can be preliminarily postulated that enlarged CNT tips yielded higher field enhancement. As for the smaller diameter obtained in floating catalyst-grown CNTs, it justifies its superior FE current density and β values over CNTs grown from pre-deposited catalyst, as presented in Table 6 - 2.

Figure 6 - 11: Simulated electric field on CNTs with (a), (c): Similar tip dimensions with CNT body; (b), (d): Enlarged tips

6.3 Summary

From the 11 – 16.7 μm heights, the pre-deposited catalyst TCVD-grown CNTs displayed increment in FE current density as the height of the CNTs hiked due to the increased CNT aspect ratio. As the height of CNT exceeded 16.7 μm , taller CNTs resulted in inferior FE current density as the structural defectiveness factor of CNTs took place, thus limiting the achievable FE current density by CNTs. In the attempt to further explore the improvement in FE current density, the FE properties of CNT grown with floating catalyst and pre-deposited catalyst TCVD techniques were compared.

From the discussed simulation and experimental results, one can conclude that the floating catalyst-grown CNTs exhibited higher FE current density than the pre-deposited catalyst-grown CNTs due to higher field enhancement at the CNT tips. Meanwhile, the higher field enhancement of floating catalyst-grown CNTs could be attributed to two possible factors: smaller CNT diameter and enlarged CNT tips. As smaller CNT diameter yielded higher CNT aspect ratio and field enhancement, it is also possible to fine-tune the CVD parameters to obtain CNTs with smaller diameter from the pre-deposited catalyst [166]. Nevertheless, the enlarged tips on the floating catalyst-grown CNTs exerted significant influence upon field enhancement, hence resulting in higher FE current density than that of pre-deposited catalyst-grown CNTs. However, other possible factors could also influence the FE properties of CNTs, such as CNT area density [167] and electrical conductivity of CNTs [159], [168], which can be subjected to future studies.

6.4 Publications

Y.D. Lim, Q. Kong, S. Wang *et al.* “Enhanced field emission properties of carbon nanotube films using densification technique”, *Applied Surface Science* – **In Press – Corrected Proof**

Y. D. Lim, D. Grapov, X. Xia *et al.* “Design and Fabrication of Carbon Nanotubes Field Emitter for Microfabricated Traveling-Wave Tube,” *IEEE Transactions on Nanotechnology* - Submitted

Chapter 7: Selective Growth of Carbon Nanotubes (CNTs) on Si/SiO₂ Structure using Floating Catalyst Chemical Vapour

Deposition Technique

The previous chapter depicted that Carbon Nanotubes (CNTs) grown using floating catalyst TCVD technique displayed superior FE properties due to high field enhancement on CNT tip. However, the growth of CNTs using such technique had been unselective, where CNTs grew all over on the Si/SiO₂ structure. Therefore, in order to integrate such CNT growth technique in the fabrication of CNT field emitter, selective growth of CNTs is required on the Si surfaces in Si/SiO₂ structure.

In this chapter, selective growth of CNTs on the Si surfaces in Si/SiO₂ structure is elaborated by using the floating catalyst TCVD technique. As a result, selective growth on Si surfaces was obtained under growth temperature of 790 °C, while the mechanism of selectivity has been discussed.

7.1 Introduction

The previous chapter depicted that CNTs grown via floating catalyst Thermal Chemical Vapour Deposition (TCVD) technique exhibited superior FE properties due to its exceptionally high field enhancement on the CNT tips. Nonetheless, it was reported that CNT films exhibited limited FE current density due to the screening effect between the CNTs [94]. Hence, in the attempt to address this issue, a widely-reported technique is to grow CNTs on isolated catalyst islands fabricated by photolithography technique to form separated CNT pillars [169], [170]. In the case of floating catalyst TCVD technique, growing CNTs in patterned form appears to be a challenge. Due to the organometallic (Fe-hydrocarbon) nature of ferrocene, the Fe content in ferrocene may act as a catalyst for the growth of CNT without the presence of an external

catalyst layer [171]. As a result, CNTs could grow non-selectively all over the fabricated structure.

Additionally, Zhang et al., [171] reported the growth of CNT on pristine Si substrates by employing the volatile catalyst source technique. The study further asserted that CNT growth was initiated by the formation of a continuous iron silicide barrier layer on the silicon substrate; the iron silicide had been postulated to reduce the contact resistance between CNTs and the Si substrate. Therefore, in order to successfully integrate ferrocene-grown CNTs in FE applications, the selective growth of CNTs in Si/SiO₂ structures is crucial. Meanwhile, Jung et al., conducted a study that performed selective growth of CNTs in Si/SiO₂ structures on SiO₂ surfaces using volatile catalyst technique. From the suggested mechanism, high selectivity of CNT growth can be achieved when a continuous layer of γ -Fe is formed on the SiO₂ layer and large clusters of FeSi₂ or FeSiO₄ are formed on the silicon surface [162]. Nevertheless, a significant drawback of this technique is the high resistivity of SiO₂ layer [172], which may increase the electrical contact resistance between CNTs and Si substrate, thus limiting its performance.

Hence, in order to attain the selective growth of CNTs on the Si surface, Labunov et al., reported the reversible selective growth of CNTs on the surfaces of either Si or SiO₂ by varying the gas dynamic factors in the CVD process. Based on the reported outcomes, reversible selective growth of CNTs could be achieved on either Si surface or 100 nm thick SiO₂ surface, depending on the gas flow rate [173]. Apart from gas dynamic factors, a rather significant factor in determining the selectivity of CNT growth on Si/SiO₂ substrates is the growth temperature. As the selectivity of CNT growth on Si/SiO₂ substrates depends heavily on the thermo-diffusivity profile of Fe particles on the Si/SiO₂ substrates, growth temperature has a significant impact upon the selectivity of CNT growth [162]. In the investigations on the temperature-dependent growth of CNTs using volatile catalyst (ferrocene/xylene) source CVD

technique, Sengupta et al., revealed improvements in the crystallinity of CNTs at higher synthesis temperatures [174]. Other than that, Bai et al., reported the temperature-dependent profile of CNT growth rate by altering the pyrolysis temperature in the CNT synthesis process [175]. However, in order to realize the integration of CNT field emitter in PH-SWS TWTA, growing CNTs selectively on the Si surfaces of Si/SiO₂ structures is definitely required.

As such, this chapter presents a comparative study on the temperature-dependence of CNT growth on pristine and 2 μm SiO₂-deposited Si substrates. The selective growth of CNTs on pristine Si substrate was achieved at 790 °C. With that, the possible mechanism of selective growth condition is further discussed in the following. By utilizing the achieved selective growth condition, CNT bundles were grown selectively at the Si surface in fabricated SiO₂ pits.

7.2 Experimental Method

CNTs were grown on 2 μm SiO₂-deposited and pristine Si substrate via Thermal Chemical Vapour Deposition (TCVD) with a floating catalyst source, as reported by Navitski et al., [102], and described in Chapter 6. A typical TCVD process was performed in a quartz tube reactor, through which 100 sccm of Argon gas flowed at varied temperatures of 760, 790, 800, 820, 840, 860, and 880 °C, under continuous injection of ferrocene/xylene solution (1 wt% ferrocene). Moreover, the growth duration was fixed at 60s. Based on the attempted growth temperatures, the selective growth of CNTs on pristine Si substrate had been attained at 790 °C. By utilizing this selective growth condition, the CNT bundles were grown in pre-fabricated SiO₂ pits. The fabrication process of the SiO₂ pits is as illustrated in Figure 7 - 1, and described in a prior study [176]. In order to fabricate the SiO₂ pits, 2 μm of SiO₂ layer was initially deposited on highly n-doped (Resistivity: 0.18 $\Omega\cdot\text{cm}$; Thickness: 300 μm) using the Plasma-Enhanced Chemical Vapour Deposition (PECVD) technique. Next, the deposited SiO₂ layer was etched selectively via photolithography and dry etching techniques, so as to form SiO₂ pits

of ~ 2 μm in diameter. Using the gained selective growth condition of CNTs, the CNT bundles were grown selectively on the exposed Si surface under the SiO₂ pits.

Figure 7 - 1: Schematic diagram of CNTs grown in Si/SiO₂ structure

The morphological, the structural (Raman), and the FE characterization conditions are similar to the details described in Sections 5.1.1 and 6.1.1.

7.3 Results and Discussion

Figure 7 - 2(a) and (b) present the Scanning Electron Microscope (SEM) images of CNT films grown on both Si and SiO₂ substrates, respectively, at 860 °C. The SEM images show that the vertically aligned CNTs were formed on both Si and SiO₂ substrates at 860 °C growth temperature. Thus, CNTs displayed significant changes in growth orientation as the

growth temperature was hiked from 790 to 860 °C. Moreover, Figure 7 - 2(a), (b), and (d), project the vertical alignment for CNTs at the growth temperature of 860 °C on both Si and SiO₂ substrates. On the contrary, at the growth temperature of 790 °C, the CNTs showed a dense lateral growth, hence resulting in a ‘spaghetti-like’ CNT morphology (Figure 7 - 2(c)). The shift in CNT alignment with growth temperature can be further explained by the mechanisms of CNT growth and alignment [177]. Fundamentally, CNTs are grown by the diffusion of carbon feedstock into catalytic nanoclusters, which are formed via thermal annealing [99]. At higher CNT growth temperatures, the catalytic nanoclusters’ size and distribution are small and homogeneous. The small and homogeneous catalytic particles result in the formation of densely-packed CNT forest, which is afflicted with high Van der Waals interaction forces between the CNT walls. The high inter-CNT Van der Waals interactions generate ‘packing’ effect upon the CNT film, thus resulting in vertical alignment. In contrast, lower CNT growth temperatures lead to the formation of relatively larger nanoclusters, hence resulting in weaker inter-CNT Van der Waals interaction and therefore, lateral growth of CNTs [128].

Figure 7 - 2: SEM images: Cross sectional view of CNTs grown on (a) Si, and (b) SiO₂ substrates at 860 °C growth temperature; plan view of CNTs grown on Si substrates at (c) 790 °C, and (d) 860 °C growth temperatures; (e) SEM image, and (f) XPS Spectra of FeSi₂

Apart from the morphological properties of CNTs, the formation of a conductive barrier layer was observed to occur at the CNT-Si interface, as illustrated in Figure 7 - 2(a). For further investigation pertaining to the CNT-Si interface, CNTs on the bare Si substrate were removed with a pair of tweezers to reveal the underneath silicide layer. The SEM image and the X-ray Photoelectron Spectroscopy (XPS) spectra of the thin layer are displayed in Figure 7 - 2(e) and (f). Figure 7 - 2(e) exhibits the formation of individual clusters on the Si substrate, which is similar to the morphological characteristics of a FeSi₂ layer, as reported by Dahal et al., [178]. For further justification, an XPS analysis was performed on the silicide layer. As illustrated in Figure 7 - 2(f), the FeSi₂ peaks emerged at the binding energies of 54.64 and 707 eV, indicating the 2p and 3p hybridization of FeSi₂. The formation of FeSi₂ hybridization peaks indicates the formation of iron silicide, which is in line with the study conducted by Ohtsu et al., [179]. The formation of FeSi₂ layer during the ferrocene/xylene pyrolysis is in agreement with Jung's et al., study, where ferrocene is initially thermally-decomposed to continuously deposit Fe

particles onto the Si substrate. Fe particles are then diffused into the Si substrate to form a continuous FeSi₂ barrier layer. When the barrier layer is formed, the subsequent Fe particles deposited on the substrate are ‘blocked’ from further diffusion into Si substrate, hence forming catalytic nanoclusters for CNT growth [162].

Figure 7 - 3: TEM images of CNTs grown on (a-b) Si; and (c-d) SiO₂ substrates at 820 °C growth temperature.

In order to further investigate the morphological properties of CNTs, the Transmission Electron Microscopy (TEM) imaging was carried out on CNTs grown on both Si and SiO₂ substrates. As displayed in Figure 7 - 3, the tubular structure of CNTs was observed on both Si and SiO₂ substrates, similar to the CNT morphology reported by Kar et al., [180]. Besides, the Multi-Walled CNT structure with a diameter of ~18 nm and ~30 nm had been noted on both Si and SiO₂ substrates, respectively. In addition, Figure 7 - 3(d) portrays that CNTs grown on

SiO₂ substrate displayed higher irregularity in CNT walls, when compared to those grown on Si substrate, which could possibly indicate the higher defectiveness of CNTs grown on SiO₂ substrates. Besides, from the CNT clusters illustrated in Figure 7 - 3(a) and (c), a detailed quantitative study on the CNT diameters grown on both Si and SiO₂ substrates had been performed, as presented in Figure 7 - 4. From the quantitative study, CNTs grown on SiO₂ substrate showed larger average diameter of 29 nm, in comparison to 18 nm on Si substrate. The larger diameter of CNTs grown on SiO₂ substrate indicated the formation of larger catalytic nanoclusters during the pyrolysis process [166]. In general, the CNT growth on Si/SiO₂ substrate via ferrocene/xylene catalyst was initiated upon formation of continuous barrier layer on the surface of the substrate via thermal diffusion of Fe particles [162]. The formation of barrier layer on the substrates significantly depends on both the thermal diffusivity and the solubility of Fe particles in the substrate [181]. Furthermore, based on the literature, Fe particles possess lower solid diffusivity on SiO₂ substrate, when compared to Si [182], [183]. Therefore, in the same CVD process, less Fe particles were found to diffuse into the SiO₂ substrate, as compared to that with Si substrate, causing more Fe particles to precipitate on the surface of the SiO₂ substrate. This led to the formation of larger catalytic nanoclusters, which could lead to the formation of CNTs with larger diameters.

Figure 7 - 4: CNT diameters distribution on Si and SiO₂ substrates at 820 °C growth temperature

Figure 7 - 5: Raman spectroscopy of CNTs grown on (a) Si, and (b) SiO₂ substrates; (c) I_d/I_g ratios of CNTs grown on Si and SiO₂ substrates

In order to further investigate the structural properties of CNTs, the Raman Spectroscopy was performed on CNTs grown on Si and SiO₂ layers (Figure 7 - 5). The emergence of D-band (1339 – 1444 cm⁻¹) and G-band (1575 – 1577 cm⁻¹) in the Raman spectra for all investigated CNT samples indicated the presence of disorder in the graphitic structure [184], as well as the in-plane vibration of C-C bond [185]. In precise, the CNTs displayed a decreasing I_d/I_g ratio, hence indicating enhanced crystallinity with increment in growth temperature. This notion is in line with that reported by Lee et al., where the degree of crystalline perfection in CNTs increased progressively with increment in growth temperature [186]. Besides, Figure 7 - 5(c) presents that the I_d/I_g ratios of CNTs grown on Si and SiO₂ substrates had been similar at 800 – 880 °C growth temperatures. The slightly higher I_d/I_g ratio of CNTs grown on SiO₂ substrates, nonetheless, could be attributed to the higher irregularity in the CNT walls, as illustrated in Figure 7 - 3.

Figure 7 - 6: CNT growth rates on Si and SiO₂ surfaces; CNT growth rate reported by Bai et al., on Si surface, at varying growth temperatures [175]

The respective CNT growth rates on both Si and SiO₂ substrates at varying growth temperatures are displayed in Figure 7 - 6. A comparison of the obtained experimental data on the CNT growth rate at varied temperatures in this study with that reported by Bai et al., [175]

had been carried out. In general, the variation of CNT growth rate with temperature exhibited a similar trend, with the growth rate reaching a maximum value at an optimum growth temperature, and a reduction as the temperature further hiked. The variances in the optimum temperature and the CNT growth could be due to the differing ferrocene/xylene concentration and gas feedstock rate [173]. From 800 to 860 °C, the CNT growth rate on Si saw increment from 10.51 to 34.28 µm/min and this decreased to 14.4 µm/min as the growth temperature was further escalated to 880 °C. At the same time, the CNT growth rate on SiO₂ increased from 6.18 to 35.77 µm/min from 800 to 840 °C, but declined to 27.04 µm/min as the growth temperature was hiked to 880 °C. Such enhancement in the growth rate at higher temperature could be attributed to the higher decomposition rate of ferrocene, which increases the catalytic effect of ferrocene [187]. Other than that, the reduction of growth rate when the temperature exceeded the optimum value could be attributed to the passivation of the Fe clusters, where hydrocarbon precursors precipitated on the catalyst particles and reduced its catalytic activity [175]. However, no CNT growth was observed at 760 °C on both Si and SiO₂ surfaces. However, at 790 °C, while insignificant CNT growth was observed on SiO₂ surface, the CNT height of ~1.25 µm was recorded for Si surface.

From the obtained selective growth condition, the mechanism of the selective growth for CNTs upon Si layer had been speculated, as portrayed in Figure 7 - 7. Fundamentally, in order to enable CNT growth, a continuous silicide layer had been required to form as a barrier layer [162], [171]. Thus, the selectivity of CNT growth largely depended on the Fe-adsorption stage on the surface [173]. At the same time, the Fe-adsorption on the surface heavily relied on the thermal diffusivity of Fe on the target surface [188]. Based on past studies, the diffusivity of Fe on Si ($\sim 10^{-6}$ cm²/s) [183] had been significantly higher than on SiO₂ surface ($\sim 10^{-14}$ cm²/s) [182] for the obtained selective growth temperature (790 °C). In addition, PECVD-grown SiO₂ displayed high porosity (~41%) [189], thus allowing more Fe particles to diffuse into the SiO₂

layer. Besides, based on the low diffusivity and the high porosity of SiO₂, it could be speculated that Fe diffused rapidly into the Si surface during the CNT growth process, and formed a continuous layer of silicide barrier layer that was also in favour of CNT growth. On the other hand, the lower diffusivity of Fe on SiO₂ surface prevented the formation of a continuous silicide layer within the short (60s) CNT growth duration. Hence, at the obtained selective growth temperature, several continuous silicide layers were formed on Si surfaces, while isolated clusters of silicide were found on SiO₂ surface. As a result, continuous CNT growth took place on Si layers, whereas unstable CNT growth was noted on SiO₂. As the temperature increased, Fe diffusivity on both Si and SiO₂ substrates increased significantly. At higher Fe diffusivity, the Fe particles gained sufficient thermal energy to diffuse into SiO₂ surface for silicide formation, which also favoured CNT growth. However, at the lower growth temperature of 760 °C, the Fe diffusivity in both Si and SiO₂ reduced, thus hindering the formation of continuous silicide layer. This explains the absence of CNTs on both Si and SiO₂ surfaces at the 760 °C growth temperature. Nevertheless, the precise mechanism of the selective growth still remains unclear, since the formation of the silicide phase on both Si and SiO₂ surfaces has yet to be completely understood, thus demanding further investigation.

Figure 7 - 7: Mechanism of the selective growth of CNTs on Si substrates

Next, the obtained selective growth condition of CNTs was employed to grow CNTs in pre-fabricated SiO₂ pits, as described in Section 7.2. Several CNT bundles were grown selectively at 790 °C on the Si surfaces of pre-fabricated SiO₂ pits on a Si substrate. The SEM images of the CNT bundles grown in SiO₂ pits are presented in Figure 7 - 8. As illustrated in Figure 7 - 8(a), an array of pits with ~ 2 μm in diameter was formed in the SiO₂ layer. Meanwhile, Figure 7 - 8(b) portrays unstable growth of CNTs on the SiO₂ layer, in line with the speculated mechanism displayed in Figure 7 - 7. Furthermore, Figure 7 - 8(c) projects vividly entangled CNTs, where a randomly aligned CNT bundle of ~ 1.25 μm high grew selectively at the bottom of the SiO₂ pit. To further justify the selective growth of CNTs on the Si layer, Raman mapping was performed on the CNT bundles that grew in the SiO₂ pits, as exhibited in Figure 7 - 8(d) and (e). Moreover, exceptionally high intensities of D-band (1339 – 1444 cm⁻¹) and G-band (1575 – 1577 cm⁻¹) were obtained from the SiO₂ pits regions, while low intensities were recorded from the SiO₂ surfaces. The low intensities of both D- and G-bands from the SiO₂ surface could occur due to the formation of amorphous carbon and

unstable growth of CNTs on the SiO₂ surface [190]. On top of that, the exceptionally high intensities of D- and G-bands on the SiO₂ pits regions pointed out the selective growth of CNTs on the Si surfaces at the bottom of the SiO₂ pits.

Figure 7 - 8: SEM Images: (a): Plane view of CNT bundles; (b) plane view, and (c): cross-sectional view of single CNT bundle. Raman map: (d) 1339 – 1444 cm⁻¹ (D-band) and (e) 1575 – 1577 cm⁻¹ (G-band)

7.4 Summary

This chapter explains the selective growth of CNTs on the Si surfaces of Si/SiO₂ structure that was carried out via floating catalyst TCVD technique. At the 790 °C growth temperature, the CNT bundles were grown selectively on the Si surface, while unstable growth of CNTs was noted on SiO₂ surfaces. The mechanism of the selectivity of CNT growth was also speculated. From the obtained selective growth condition, CNTs were grown in isolated

bundles, thus forming CNT field emitter array (FEA). The fabrication of CNT FEA is further described in the next chapter.

7.5 Publication

Y.D. Lim, L. Hu, A.V. Avramchuck *et al.*, “Temperature-dependent selective growth of carbon nanotubes in Si/SiO₂ structures for field emitter array applications,” *Materials Research Bulletin*, vol. 95, pp. 129–137, 2017

Chapter 8: Fabrication of Carbon Nanotubes (CNTs) Field Emitter Array

The previous chapter shows that the selective growth condition of Carbon Nanotubes (CNTs) on the Si surfaces of Si/SiO₂ structures was obtained at 790 °C growth temperature via floating catalyst TCVD technique. However, at 790 °C, the CNTs exhibited random alignment to form CNT bundles, which could potentially affect the overall field enhancement of CNTs, hence resulting in inferior FE properties.

Hence, in this chapter, the CNTs bundles obtained at 790 °C growth temperature were confined by using pre-fabricated SiO₂ pits. The improvement of FE current density in CNT bundles upon confinement with pits for varied diameters was also investigated.

8.1 Introduction

The CNTs can be grown selectively on the Si surfaces of Si/SiO₂ structure, as demonstrated in the previous chapter. Nonetheless, as portrayed in Figure 7 - 8, CNTs exhibited random alignment under selective growth temperature (790 °C), hence forming CNT bundles on Si surfaces. In the case of growing CNT bundles on pre-patterned catalyst islands, these CNTs were spread out under random alignment, as shown in Figure 8 - 1. Such spreading out that formed CNT bundles with lower aspect ratio may eventually affect the field enhancement in CNTs. As a result, spread out CNT bundles exhibited inferior FE properties in accordance to their low aspect ratio [20], [94]. In this case, since floating catalyst TCVD-grown CNTs can be selectively obtained on the Si surfaces of Si/SiO₂ structure, a possible solution is to confine them in fabricated pits so as to increase their overall aspect ratio. Upon confinement, the CNT bundles with higher aspect ratio had been speculated to possess higher field enhancement, thus resulting in higher FE current density.

Figure 8 - 1: Schematic diagram of vertically-aligned CNTs and random-growth of CNTs

In this chapter, the improved FE properties of random-growth CNT bundles by confining them in microfabricated SiO₂ pits are looked into. In fact, it was discovered that CNT bundles confined in SiO₂ pits attained higher FE current density, in comparison to free-standing CNT bundles. Such higher FE current density could be attributed to the higher aspect ratio of CNT bundles confined in SiO₂ pits, which enhances their FE properties.

8.2 Experimental Method

Figure 8 - 2(a) illustrates the fabrication process of CNT arrays, as described in Section 7.2. In a typical fabrication flow, SiO₂ was initially deposited on highly n-doped Si substrates (Resistivity = $\sim 0.018 \Omega\cdot\text{cm}$) via PECVD technique (Figure 8 - 2(a)(i)). Next, the deposited SiO₂ layer was structured via photolithography and selective dry etching to reveal the underneath Si layer (Figure 8 - 2(a)(ii)). Finally, CNTs were grown on the structured substrates

via Thermal Chemical Vapour Deposition (TCVD) method with floating catalyst source (ferrocene/xylene mixture) (Figure 8 - 2(a)(iii)). The growth time of 1 min was opted to obtain CNT bundles of 1~2 μm in height, which could be fully confined within 2 μm depth in SiO_2 pits. As a baseline study, the freestanding CNT bundles, as shown in Figure 8 - 2(b)(i), were also prepared to compare their FE properties against those of CNT bundles confined in SiO_2 pits. Furthermore, in the attempt to better distinguish the respective CNT samples investigated in this chapter, the SiO_2 thickness and the diameter of SiO_2 pits had been varied to form Samples A, B, and C. The schematic diagram and the specifications of Samples A, B, and C are presented in Figure 8 - 2(b) and Table 8 - 1, respectively.

Figure 8 - 2: (a) Fabrication Process of CNT Samples; (b) Schematic diagram of (i) Sample A, (ii) Sample B, and (iii) Sample C

Table 8 - 1: Sample specifications

Sample Type	Sample Description
Sample A	Free-standing CNT bundles
Sample B	CNT bundles confined in 2 μm diameter SiO ₂ pits
Sample C	CNT bundles confined in 0.5 μm diameter SiO ₂ pits

The morphological and the structural (Raman) details are as described in Sections 5.1.1 and 6.1.1. The FE measurement was carried out in 10^{-4} Pa with pulsed voltage source, as described in Sections 5.1.1 and 6.1.1. Additionally, the cathode-anode distance was estimated to be at 25 μm , while the cathode area of 0.75 mm^2 had been estimated in the measurement.

8.3 Results and Discussion

Figure 8 - 3 illustrates the SEM images of Samples A, B, and C. The CNT bundles grown selectively were revealed on the Si layer underneath the SiO_2 layer. In fact, sparse and unstable CNT growth had been observed on the SiO_2 layer, as depicted in Figure 8 - 3(c) and (e). Moreover, the presence of unstable CNT growth on SiO_2 layer had been expected, as explained in the previous chapter. Since 2 μm SiO_2 exhibited low electrical conductivity, the unstable CNT growth on SiO_2 surface possessed negligible FE current [172]. Hence, it could be postulated that most electrons were emitted from the CNT bundles grown on Si surfaces. Meanwhile, the SEM images of Sample A are presented in Figure 8 - 3(a), where the magnified SEM images of individual CNT bundle are presented in the inset of Figure 8 - 3(a) and (b). These magnified SEM images show that the CNTs were randomly aligned and spread out to generate CNT bundles. The formation of random growth CNTs, thus, could be attributed to the low Van der Waals force between the CNTs [99], [128] so as to form spread out bundles. As a result, the CNT bundles were spread out to generate bundles with larger diameter ($\sim 2.7 \mu\text{m}$), in comparison to that of the fabricated SiO_2 pits ($\sim 2 \mu\text{m}$), as described in Figure 8 - 1.

Figure 8 - 3: SEM images of: (a), (b) Freestanding CNT bundles (Sample A); (c), (d) CNT bundles grown in 2 μm diameter SiO₂ pits (Sample B); (e), (f) CNT bundles grown in 0.5 μm diameter SiO₂ pits (Sample C)

In the attempt to confine the CNTs, the bundles were grown in microfabricated SiO₂ pits, as shown in Figure 8 - 3(c) – (f). As for Sample B, which is presented in Figure 8 - 3(c), the CNTs were grown selectively at the bottom of the SiO₂ pits. A clearer view of the CNT bundle is portrayed in the inset of Figure 8 - 3(c), where the magnified SEM images of individual CNT bundle grown in 2 μm diameter SiO₂ pit are presented. These CNTs exhibited random growth orientation, which is similar to that of Sample A. From the cross-sectional image of individual CNT bundle in Sample B, one can observe that the SiO₂ layer is slightly

under-etched to reduce the area of the exposed Si layer. Moreover, upon confining by the SiO₂ pit, the base diameter of the CNT bundles had been reduced significantly to 1.5 μm in Sample B (Figure 8 - 3(d)), in comparison to Sample A. In addition, the height of the CNT bundles had been estimated to be $\sim 1.2 \mu\text{m}$. Besides, the reduction of the base diameter of CNT bundles could be attributed to the confinement by SiO₂ pits.

To further confine the CNT bundles, the SiO₂ pits of $\sim 0.5 \mu\text{m}$ diameter had been employed to contain the CNT bundles. After further confinement of the CNT bundles, a near-cylindrical structure was found to be confined in narrow ($\sim 0.5 \mu\text{m}$ diameter; $\sim 2 \mu\text{m}$ depth) SiO₂ pits, as displayed in Figure 8 - 3(e) and (f). The CNT bundle height showed uneven distribution of ~ 1 to $1.8 \mu\text{m}$ height due to the random growth nature of the CNTs. Besides, under the confinement of $0.5 \mu\text{m}$ diameter SiO₂ pits, the CNT bundle adhered to the shape of the pits with its diameter further confined to $0.5 \mu\text{m}$. Such shift in the CNT bundle diameter may yield higher FE properties, as discussed in the latter part of this chapter.

For $2 \mu\text{m}$ diameter SiO₂ pits, CNT bundles show similar I_d/I_g ratio at inter-pit separation distance between $4 - 10 \mu\text{m}$ as reported in ref. [127]. Therefore, it can be speculated that the period and diameter of the pits have minimal influence on the properties of CNT grown on the Si surface. However, it is possible that the height of the pits can affect the properties of CNTs grown on both Si/SiO₂ surfaces. As reported by Cao et al., the SiO₂ thickness can affect the properties of CNTs grown on its surface using floating catalyst TCVD technique [191]. As the pits are structured by SiO₂, changing the thickness of SiO₂ (which changes the pit's height) can affect the properties of CNTs.

Figure 8 - 4 (a-d): TEM images of CNTs grown by floating catalyst TCVD technique (790 °C selective growth condition)

So as to further investigate the morphological properties of CNTs, the Transmission Electron Microscopy (TEM) study was performed on the CNTs, as presented in Figure 8 - 4. The typical diameter of the CNTs obtained in this study had been varied between 14 and 24 nm. At the same time, a multi-walled structure was observed on the CNTs, as labelled in Figure 8 - 4(d). Besides, the presence of CNTs with larger diameter (24 nm), in comparison to CNTs grown at 820 °C (Figure 6 - 9 and Figure 7 - 3), could be attributed to the lower growth temperature that resulted in the formation of larger catalyst particles for CNT growth, as revealed by Aksak et al., [192]. Furthermore, from the TEM images, several multi-walled structures were observed on the CNTs. Since several studies have reported the achievement of high FE current density ($> 1 \text{ A/cm}^2$) by MWCNTs [100], [103], [107], one can presume that the

MWCNTs obtained in this study is indeed suitable to fabricate CNT emitters in delivering sufficient current density ($\sim 1 \text{ A/cm}^2$), as required by vacuum electronic applications.

The FE measurements of Samples A and B are shown in Figure 8 - 5 and Figure 8 - 6, respectively. From the FE measurement of Sample A, the turn-on field of $30.6 \text{ V}/\mu\text{m}$ was obtained at the initial FE of 0.5 mA/cm^2 . At the same time, Sample A attained maximum current density of 76.9 mA/cm^2 under $49.7 \text{ V}/\mu\text{m}$ electric field. Other than that, a significant improvement in FE properties was noted on Sample B, in comparison to Sample A. Besides, as presented in Figure 8 - 6, under the same inter-pit separation distance of $4 \mu\text{m}$, Sample B exhibited lower turn-on field of $16 \text{ V}/\mu\text{m}$ at the similar FE current density of 0.5 mA/cm^2 , when compared to Sample A. At the same time, Sample B also achieved higher FE current density of 333.33 mA/cm^2 under electric field of $21.4 \text{ V}/\mu\text{m}$. Nonetheless, at larger inter-pit separation distance, higher electric field would be required to meet a similar FE current density of $> 300 \text{ mA/cm}^2$, hence leading to lower FE current density at similar applied electric field. Furthermore, it was reported that an optimal condition of $R/H > 2$ had been required to minimize the screening effect between CNTs, in which R and H represent the separation distance between CNTs and the CNT height, respectively [155], [193]. Furthermore, as exhibited in Figure 8 - 3(d), since the estimated height of the CNT bundle had been $\sim 1.2 \mu\text{m}$, the investigated separation distances of 4, 6, 8, and $10 \mu\text{m}$ fulfilled the $R/H > 2$ condition, pointing out that the screening effect between the CNT bundles had minimized [170]. Hence, the FE current density at larger inter-pit distance could be attributed to the presence of limited CNT bundles per unit area. As the number of CNT bundles per unit area is reduced, less electrons are emitted per unit area, hence reducing FE current density. With that, higher electric field is needed to achieve a similar FE current density of $> 300 \text{ mA/cm}^2$ as the inter-pit distance increases.

Figure 8 - 5: (a) FE measurement of Sample A

Figure 8 - 6: FE measurement of Sample B at varied separation distances between SiO_2 pits

The FE measurements of Sample C at varying inter-pit separation distances are portrayed in Figure 8 - 7(a). Sample C recorded FE current density of $1 - 1.4 \text{ A/cm}^2$ at separation distances that range between 0.5 and $7 \mu\text{m}$. The slight variation in the maximum achievable FE current density could be attributed to the uneven heights of CNT bundles, as shown in Figure 8 - 3(e) and (f). From the FE measurements, one can observe that Sample C with $4 \mu\text{m}$ inter-pit distance exhibited optimal FE properties. The achievement of such optimal FE properties at $4 \mu\text{m}$ inter-pit distance could be attributed to its optimal R/H ratio, as discussed earlier. Under the same separation distance of $4 \mu\text{m}$, Sample C exhibited significantly lower turn-on field of $11 \text{ V/}\mu\text{m}$ to gain initial FE current density of 0.5 mA/cm^2 , in comparison to

Sample A (30.6 V/ μm) and Sample B (21.4 V/ μm). Meanwhile, Sample C (4 μm separation) also attained FE current density of 1.24 A/ cm^2 under 24.4 V/ μm electric field, which is significantly higher than Samples A (76.9 mA/ cm^2) and B (333.33 mA/ cm^2). Nevertheless, it had been discovered that the electric field had to achieve FE current of ~ 1 A/ cm^2 when the inter-pit separation distance was shifted from 0.5 to 7 μm . Furthermore, as illustrated in Figure 8 - 7(b), the 4 μm distance required the lowest electric field to achieve 1 A/ cm^2 FE current density. As the separation distance was reduced to below 4 μm , higher electric field was sought to achieve the 1 A/ cm^2 current density. This could be due to the screening effect that takes place between the CNT bundles, where the investigated separation distances of 0.5 and 3.0 μm do not fulfil the $R/H > 2$ optimal condition. Nonetheless, at larger separation distances that exceed 4 μm , higher electric field is required to achieve similar FE current density of ~ 1 A/ cm^2 . This could be attributed to the reduction of CNT bundles per unit area, as discussed earlier.

Figure 8 - 7: (a) FE measurements, and (b) Electric field to achieve 1 A/ cm^2 FE current density, for Sample C at varying inter-pit separation distances

Figure 8 - 8 displays the FE measurements and the Fowler Nordheim (FN) plots of Samples A, B, and C at the same inter-pit separation distance of 4 μm ; while Table 8 - 2 tabulates the FE properties of these respective samples. Figure 8 - 8(a) further portrays that Sample C had managed to attain the highest FE current density (1.24 A/ cm^2) among the investigated samples, followed by Sample B (333.33 mA/ cm^2), and Sample A (76.9 mA/ cm^2).

At the same time, the FN plots of Samples A, B, and C presented in Figure 8 - 8(b) show a linear trend, which indicates that these samples adhere to the well-established FN theory [194]. Furthermore, based on the slopes of the FN plots, the field enhancement factors (β) of Samples A, B, and C had been determined to be 1948.57, 2705.36, and 5780.07, respectively. The higher β value recorded in Sample C is in line with its higher FE current density. Besides, the higher β value and its associated FE current density, as recorded by Sample C, could be attributed to its geometrical shape. Moreover, Utsumi asserted that the cylindrical-shaped field emitter possesses better field enhancement, when compared to pyramidal-shaped or widened and spread out emitters [19], [74]. By comparing Figure 8 - 3(d) and (f), the CNTs in Samples A and B exhibited randomly-grown bundles, while CNTs in Sample C were confined into cylindrical-shapes. Furthermore, such cylindrical-shaped CNT bundles in Sample C had been proven to yield higher field enhancement, as reflected by its calculated β value, which is in agreement with that suggested by Utsumi [74].

Figure 8 - 8: (a) FE measurements, and (b) FN plots of Samples A, B, and C at the same inter-pit separation distance of 4 μm

Table 8 - 2: FE properties of Samples A, B, and C at 4 μm inter-pit separation distance (Summarized)

Sample	Turn-on field to obtain 0.5 mA/cm ²	Maximum FE current density@ Applied Field	Field Enhancement Factor (β)
A	30.6 V/ μm	76.9 mA/cm ² @49.7 V/ μm	1948.57
B	16 V/ μm	333.3 mA/cm ² @21.4 V/ μm	2705.36
C	11 V/ μm	1.24 A/cm ² @24.4 V/ μm	5780.07

To further understand the FE properties of the investigated CNT samples, we have performed emission stability test on Sample A, B, and C over ~1 hour of continuous emission. Electric field of approximately 50 V/ μm , 21 V/ μm , and 24 V/ μm are applied onto Sample A, B, and C, respectively, to obtain similar current associated with the current density obtained and presented in Table 8 - 2. The emission current of Sample A, B, and C for 1 hour is presented in Figure 8 - 9. Generally, CNT emitters (Sample A, B, and C) show fluctuating emission current over 1 hour continuous emission. This unstable current emission can be attributed to several reasons, such as heat-induced damages on the CNTs during emission [101], foreign ionic adsorbates damaging [195], [196]. For foreign ionic adsorbates damaging, there are possibly residual organic binders on CNTs after growth, which can be ionized by emitting electrons and collides on CNTs, which causes damages onto CNT emitter [106]. Besides the abovementioned reasons, a possible reason of the unstable current emission can be attributed to random growth nature of CNTs. As discussed in a previously-reported study, the non-uniform height of CNTs causes uneven distribution of electric field, which results in unstable emission current [197]. In the case of randomly-grown CNTs confined in SiO₂ pits, the CNT bundles have uneven heights, as shown in Figure 8 - 3. This can result in unstable emission current induced by uneven electric field distribution.

Figure 8 - 9: Emission current of CNT samples over ~1 hour continuous emission under different applied field: (a) Sample A (50 V/μm), (b) Sample B (21 V/μm), and (c) Sample C (24 V/μm)

From Figure 8 - 9(a), Sample A shows fluctuating emission current within the range of 378 to 579 μA over 1 hour continuous emission. This fluctuation feature is similar to a previous study reported by Prudnikava et al [102]. This fluctuation can be attributed to various factors, as

discussed earlier. At the beginning 100s of the continuous emission, despite significant fluctuation of emission current, average FE current of $\sim 570 \mu\text{A}$ ($\sim 76 \text{ mA/cm}^2$) is obtained, similar to the FE current density of Sample A presented in Table 2 ($\sim 76.9 \text{ mA/cm}^2$). As the emission continues, the emission current reduces gradually to the range of $400 \sim 500 \mu\text{A}$, reduces up to $\sim 30\%$ from the original current value of $\sim 570 \mu\text{A}$ at the first 5 min. This can be attributed to the partial degradation of CNTs under uneven field distribution, where significant fraction of CNTs with relatively high localized field are burnt-off during emission [134]. For Sample B, the current fluctuates from 2412 to $2499 \mu\text{A}$ with average emission of $\sim 2548 \mu\text{A}$ ($\sim 340 \text{ mA/cm}^2$), similar to the FE current density of Sample B presented in Table 2 (333 mA/cm^2).

As compared to Sample A, Sample B does not exhibit any significant reduction in average FE current over 1 hour continuous emission. Besides, despite several instances of sudden reduction in emission current, the current emission from Sample B deviates $3 - 8 \%$ from the average value of $2548 \mu\text{A}$, showing higher consistency and emission stability than Sample A. The sudden reduction in emission current can be attributed to attributed foreign ionic adsorbates damaging or high localized field CNTs burning-off [195], [196]; whereas the higher emission stability can be due to higher uniformity in electric field distribution in CNT bundles. As the CNT bundles are confined in SiO_2 pits, the bundles are less spread-out as illustrated in **Error! Reference source not found.**(b), which possible result in uniform electric field distribution and better emission stability as compared to freestanding CNT bundles in Sample A.

Meanwhile, for the continuous current emission of Sample C under applied field of $24 \text{ V}/\mu\text{m}$ (Figure 8 - 9(c)), its emits $\sim 9000 \mu\text{A}$ current (1.2 A/cm^2) for the first $\sim 600\text{s}$, similar to the FE measurement obtained and presented in Table 8 - 2 (1.24 A/cm^2). However, after 600s continuous emission, the emission current experienced a sudden drop from ~ 9000 to $\sim 8205 \mu\text{A}$. This can be attributed to the damaging of high electric field CNT bundles. As observed in

Figure 8 - 3, CNTs protruding out from the SiO₂ pits are observed on Sample C. These protruding CNTs exhibit high localized electric field due to the reduced screening effect from neighbouring CNT bundles [138], [155], as discussed earlier. However, the high field enhancement on protruding CNTs will result in higher current density flown in the protruded CNTs as compared to the confined CNTs, which can cause structural damages and sudden failure during continuous emission [198]. In the case of Sample C, a significant fraction of the protruded CNTs may undergo structural damages during continuous emission, which causes the sudden drop in emission current from ~9000 to ~8205 μA . Nevertheless, after the sudden drop in emission current, Sample C shows relatively stable emission current. The emission current fluctuates between 8032 to 8512 μA the next ~3000s, which deviates 4 – 6 % from the average emission current of ~8205 μA . Besides, the stabilized emission current of ~8205 μA corresponds to 1.09 A/cm^2 FE current density, which falls within the range of 1 – 1.4 A/cm^2 FE current density as measured. The obtained stabilized current density of 1.09 A/cm^2 partially fulfils the operation requirement of vacuum electronic devices as suggested by Wang et al. [14], [15] as mentioned earlier, which demonstrates the promising potential of SiO₂ pits-confined CNT bundles in vacuum electronic applications.

8.4 Summary

In this chapter, several separated CNT bundles were grown on Si/SiO₂ structure by using the selective growth condition determined in the previous chapter. As such, the free-standing CNT bundles achieved FE current density of 76.9 mA/cm^2 . For further enhancement in FE current density, the CNT bundles were confined by SiO₂ pits. In precise, the CNT bundles that were confined by 2 μm diameter SiO₂ pits achieved FE current density of ~333.3 mA/cm^2 , while bundles confined by 0.5 μm diameter SiO₂ pits attained FE current density of 1 – 1.4 A/cm^2 . Both FE measurements and FN plots of the samples showed that confining CNT

bundles in narrower (0.5 μm diameter) SiO_2 pits yielded higher FE current density due to higher field enhancement. By combining these outcomes, it can be concluded that confining random growth CNT bundles can indeed yield higher FE current density.

8.5 Publication

Y. D. Lim, D. Grapov, L. Hu *et al.* “Enhanced Field Emission Properties of Carbon Nanotube Bundles Confined in SiO_2 pits,” *Nanotechnology* – **Accepted**

Chapter 9: Field Emission (FE) Properties of Screen-Printed Carbon Nanotubes (CNTs) Field Emitter

From the previous chapter, the Carbon Nanotube (CNT) bundles confined in SiO₂ pits exhibited FE current density of 1 – 1.4 A/cm². Hence, in order to achieve signal gain of > 20 dB in PH-SWS TWTA, higher FE current density is desired.

Therefore, in this chapter, further improvement in FE current density is explored by using screen-printed CNTs. CNTs were mixed with nanoparticle additives and adhesives to enhance their electrical properties and electrical contact on the substrate. The FE current density in the range of A/cm² had been obtained consistently, as a result, from the screen-printed CNTs.

9.1 Introduction

From the previous chapter, the FE current density of 1 – 1.4 A/cm², which had been obtained from CNT bundles (grown via floating catalyst TCVD technique), was confined in 0.5 µm SiO₂ pits. This corresponded to the 7.5 – 10 mA emission current under the 0.75 mm² cathode area. This range of emission current had been expected to deliver signal gain at approximately 20 ~ 25 dB in PH-SWS TWTA, as displayed in Figure 4 - 3. Nonetheless, due to the random growth nature of floating catalyst-grown CNTs, its FE current density exhibited a certain degree of uncertainty. This is shown in Figure 8 - 7, where the CNT bundles that were confined by 0.5 µm SiO₂ pits emitted FE current density from 1 – 1.4 A/cm².

It has been discussed that CNTs with higher aspect ratio yielded higher FE current density due to higher field enhancement at CNT tips [94]. This variation of CNT aspect ratio, along with its corresponding FE properties, is also demonstrated in Chapters 5 and 6. Nevertheless, apart from the high aspect ratio, the electrical conductivity and the substrate adhesion of CNTs also have been noted to play significant roles in its corresponding FE

properties. CNTs with high substrate adhesion offer better electrical contact between CNTs and substrate, which could result in better FE properties [199].

Therefore, in order to achieve high FE current density, Lei et al., have demonstrated high FE current density (11.2 A/cm^2) using screen-printed CNTs. In the reported work, Bismuth powder, ethy cellulose, and terpineol were mixed with CNTs to enhance its adhesion and electrical conductivity, which fulfilled the abovementioned conditions so as to achieve high FE current density [107]. Aside from high FE current density, a gate electrode was also required to extract the electrons from the CNTs by using applied electric field [200], [201]. From the same study reported by Lei et al., a metallic mesh with rectangular openings had been used. Since electron collision on mesh is unavoidable in the FE process [202], fine-tuning on the mesh structure is essential to maximize the number of electrons emitted from the mesh [203], as well as to minimize the number of electrons that collide on the mesh structure.

Hence, this chapter looks into the FE properties of screen-printed CNT field emitter. The CNT paste was first synthesized and printed onto the Si substrate by using the screen-printed technique. As a comparative study, the screen-printed CNTs with emitter areas of $0.5 \times 1 \text{ mm}$, $1 \times 2 \text{ mm}$, and $2 \times 4 \text{ mm}$ had been synthesized and their respective FE properties are studied.

9.2 Experimental Method

CNT paste was screen-printed onto highly n-doped Si substrates to synthesize the CNT field emitter. Single-walled CNTs (SWCNTs, purchased from Nanjing XFNANO Materials TECH Co.) were used as electron emitters. In preparing the CNT paste, 0.3g of CNTs, 0.3g of Ni, and 0.3g of ITO nanopowders were added to 15g of terpinenol solvent and ball-milled for 50 min. Next, 0.8g of ethyl cellulose binder was added and ball-milled again for 100 min. The obtained CNT paste was then printed onto Si substrate by using a patterned screen, so as to form rectangular cathodes with dimensions of $0.5 \times 1 \text{ mm}$, $1 \times 2 \text{ mm}$, and $2 \times 4 \text{ mm}$,

respectively. The as-printed cathodes were dried at 200°C in air for an hour, followed by 700°C annealing in vacuum with base-pressure of 10^{-4} Pa. Finally, the CNT cathodes were mechanically activated by using the conventional adhesive tape method with 3M scotch tape with no trace left. The schematic diagram describing the synthesis process and the photograph of screen-printed CNT emitters are presented in Figure 9 - 1.

Figure 9 - 1: Fabrication process and dimensions of screen-printed CNT field emitter

The morphological and the structural (Raman) details are as described in Sections 5.1.1 and 6.1.1. The FE measurement was carried out in 10^{-6} Pa with pulsed voltage source, as described in Section 7.2. Besides, cathode areas of 0.5×1 mm, 1×2 mm, and 2×4 mm are investigated in this chapter.

9.3 Results and Discussion

Figure 9 - 2(a) and (b) display the SEM images of screen-printed CNTs. Figure 9 - 2(a) depicts the agglomeration of nanoparticles, which had been found to co-exist with CNTs. The agglomeration of particles could be speculated to occur during the ball-milling process of CNT-particles mixture. Nevertheless, since CNTs existed in high abundance, as observed in Figure 9 - 2(a), the presence of these agglomerates had been expected to exert minimal influence on the overall FE properties of the printed CNTs. At higher magnification (Figure 9 - 2(b)), the nanoparticles were found to be decorated on the CNT bodies. The morphology of these particles-decorated CNTs is, in fact, similar to the reported literature that asserted enhancement of CNT's FE properties by metal particles decoration [107], [204], [205]. To further comprehend the morphological properties of CNTs, the TEM image of a single CNT had been captured, as illustrated in the inset of Figure 9 - 2(b). The image shows the CNT with single-walled structure, where the CNT diameter was ~ 5 nm. This ~ 5 nm diameter measurement is smaller than that of the floating catalyst-grown CNTs, which is 14 – 24 nm diameter, as retrieved in Chapter 8, which could be expected to exhibit superior FE properties. Furthermore, in order to verify the single-walled structure of CNTs, Raman spectroscopy was performed (Figure 9 - 3). The predominant peak located at 1587.6 cm^{-1} corresponded to G-band (C-C sp^2 bonds), while the weak peak at 1344.3 cm^{-1} was associated to D-band (C-C sp^3 bonds) [157], [206]. The obtained Raman spectra present the typical features of single wall CNTs [184].

Figure 9 - 2: SEM images of screen-printed CNTs under (a) 50000 $\times$ magnification, and (b) 100000 $\times$ magnification (inset: TEM image of single CNT)

Figure 9 - 3: Raman Spectrum of screen-printed CNTs

The FE measurements of the screen-printed CNT field emitter are presented in Figure 9 - 4. As a baseline study, the FE properties of both pristine CNTs and CNTs mixed with ITO and Ni particles of 2 $\times$ 4 mm CNT field emitter had been compared, as illustrated in Figure 9 - 4(a). From the FE measurements, it was revealed that the achievable FE current density by CNTs displayed an increment from 2.12 to 3.43 A/cm² upon addition of Ni and ITO nanoparticles. The drastic improvement in the FE properties of screen-printed CNTs as compared to confined CNT bundles presented in Chapter 8 can be attributed to several factors. First, the CNTs used in screen-printed emitter has much smaller diameter of $\sim$ 5 nm as compared to floating catalyst-grown CNTs ($\sim$ 14 nm). Besides, the improvement in current density, could

be attributed to the enhancement of substrate adhesion and electrical properties of CNTs. The addition of ethyl cellulose improves the substrate adhesion of CNTs, whereas the addition of Ni and ITO nanoparticles improve the electrical properties of CNTs, leading to improved FE properties. The details of this enhancement is discussed in a prior work carried out by Chen et al., [108].

Figure 9 - 4: FE Measurements of: (a): Pristine CNTs, and CNTs with ITO/Ni additives (2×4 mm dimension); and (b) CNTs field emitter (with additives) of varying dimensions

In the attempt to further explore the improvement in the FE current density of CNT field emitter, the dimension of the emitter was reduced from 2×4 mm to 1×2 mm, and 0.5×1 mm, respectively. The FE measurements of emitters with the abovementioned dimensions are presented in Figure 9 - 4(b). Under similar ~ 11 V/μm applied electric field, the FE current density of CNT emitter witnessed an increment from 3.75 to 7.5 A/cm² as the dimension was reduced from 2×4 mm to 1×2 mm, while the current density was further increased to 11.2 A/cm² as the dimension was further reduced to 0.5×1 mm. Besides, so as to ensure the repeatability of FE current density, repeated FE measurements had been performed on the investigated emitter dimensions, as illustrated in Figure 9 - 5(b). It was observed that the CNTs did undergo inconsistent FE behaviour at the 1st/2nd voltage sweep due to the possible inhomogeneity in printed CNT paste, which apparently, caused some CNTs to burn off [137].

From the 3rd sweep onwards, the CNTs exhibited consistent FE current density of 9 A/cm², 3.75 A/cm², and 2 A/cm² for 0.5 × 1 mm, 1 × 2 mm, and 2 × 4 mm dimensions, respectively.

Figure 9 - 5: Repeated FE Measurements on CNT field emitter (with additives) of (a) 0.5 × 1 mm, (b) 1 × 2 mm, and (c) 2 × 4 mm

A possible cause for the increase in FE current density upon scaling down of emitter area had been the increase in localized electric field on the surface of screen-printed CNTs. Moreover, it was reported that the localized electric field at the edges of the emitter was significantly higher than that of the centre [207]. As for smaller rectangular emitter, it could be postulated that the electric field at the edges may induce more significant effect on the overall field enhancement of the emitter [207], thus resulting in higher FE current density [153]. Thus, in order to justify this postulation, the localized electric field of CNT field emitters (0.5 × 1, 1 × 2, and 2 × 4 mm dimensions) had been simulated under the same applied field of 11 V/μm

using CST PARTICLE STUDIO SUITE®. The electric field distribution on the CNT field emitter is illustrated in Figure 9 - 6. All the three investigated dimensions of the CNT emitter exhibited higher electric field at the edges, thus aligning well with prior studies [208], [209]. At the same time, the electric field on the emitter surface increased as the dimension of the CNT emitter reduced from 2×4 mm to 0.5×1 mm, which is in agreement with the postulation exerted earlier.

Figure 9 - 6: Simulated electric field on CNT emitter of various dimensions (along w-direction as presented in Figure 9 - 1)

9.4 Summary

From the obtained FE measurements, high FE current density in the range of A/cm^2 had been obtained for all 2×4 mm, 1×2 mm, and 0.5×1 mm emitter dimensions. This could have been due to several factors, including enhanced electrical properties of CNTs by Ni and ITO additives, as well as the enhanced substrate adhesion by Ethyl Cellulose adhesive, which corresponded to improve the substrate electrical contact and the FE properties of CNTs. Since 0.5×1 mm emitter achieved the highest FE current density of 9 A/cm^2 consistently, its FE measurement outcomes are applied as the baseline for the design and the simulation of CNT field emitter, as discussed in the next chapter.

9.5 Publication

Y. D. Lim, J.T. Chen, C.B. Yan *et al.* “Hexagonal Mesh Screen-Printed Carbon Nanotubes Field Emitter for Microfabricated Traveling Wave Tube”, *IEEE Transactions on Electron Devices* - **Submitted**

Chapter 10: Design and Simulation of Hexagonal Mesh Screen-Printed CNT Field Emitter

From the previous chapter, a FE current density of 9 A/cm^2 was obtained consistently from $0.5 \times 1 \text{ mm}$ rectangular screen-printed Carbon Nanotubes (CNTs), which corresponded rather well to 45 mA emission current. The obtained emission current is theoretically sufficient to achieve $> 20 \text{ dB}$ signal gain in PH-SWS TWTAs. However, to completely utilize the screen-printed CNTs in PH-SWS TWTAs, a mesh had been required to extract the electrons from the CNTs.

With that, in this chapter, a hexagonal mesh is designed and optimized to integrate CNT field emitter into PH-SWS TWTAs. In Section 10.2, the geometrical shape of the hexagonal mesh is designed and optimized. In Section 10.3, the obtained FE properties of screen-printed CNTs under the hexagonal mesh are integrated into the PH-SWS TWTAs to simulate its signal gain performance in the TWTAs.

10.1 Introduction

From the previous chapter, high FE current density of 9 A/cm^2 was obtained consistently from screen-printed CNTs, which corresponded to 45 mA from $0.5 \times 1 \text{ mm}$ cathode area. This obtained FE current is theoretically sufficient to yield $> 20 \text{ dB}$ signal gain in PH-SWS TWTAs, as simulated in Chapter 4 and presented in Figure 4 - 3. Nevertheless, to completely utilize the screen-printed CNTs in PH-SWS TWTAs, a mesh structure had been required to extract the electrons into the PH-SWS, as portrayed in Figure 10 - 1. With that, a plane anode was employed to obtain the FE measurements of screen-printed CNTs, as reported in Chapter 9. Despite of the high current density of 9 A/cm^2 obtained, the electrons failed to escape from the plane anode into the PH-SWS. As a result, no signal gain could be generated

if such setup is used in PH-SWS TWTA. Therefore, in order to address this issue, a mesh structure is required to apply the necessary electric field on CNTs for electron emission, yet enabling the electrons to escape from the mesh and travel into the PH-SWS.

Figure 10 - 1: Schematic diagrams of plane anode measurement system and CNT field emitter with mesh structure

In designing the mesh, the aim is to obtain sufficient electrons escaping from the mesh structure for signal amplification in PH-SWS TWTA, yet minimizing collision among the electrons on the mesh to reduce heat-induced damages on it [210]. So as to maximize electron emission, high localized electric field has to be induced by the mesh for better field enhancement, which is in accordance to Fowler-Nordheim (FN) theory [126]. It has been reported that sharp corners exhibit higher field intensity than smooth, rounded surface [211]. Therefore, a polygon-shaped mesh structure (triangle, square, pentagon etc.) is preferred over rounded-shape mesh structure. In this study, a mesh structure with hexagonal openings had been employed as the main design.

In this chapter, a hexagonal mesh structure had been designed and simulated to be integrated into the screen-printed CNTs. The FE properties of the hexagonal mesh screen-printed CNT field emitter were also simulated to obtain the FE current emitted from the mesh

structure. By using the obtained FE behaviour, its signal amplification performance in PH-SWS TWTA was simulated.

10.2 Design and Simulation of Hexagonal Mesh

In order to perform PIC simulation on the FE properties of CNTs under hexagonal mesh, 2 simplified models were built to compare the FE performances of CNTs under planar anode and hexagonal mesh, as presented in Figure 10 - 2.

Figure 10 - 2: Simplified models: Orthogonal and cross-sectional views of CNT emitters with (a) & (c): plane anode; (b) & (d): hexagonal mesh, respectively.

In approximating the actual FE measurement condition, the anode-cathode distance, along with its potential difference, had been fixed at $\sim 300 \mu\text{m}$ and 3300 V, respectively, as displayed in Figure 10 - 2(c) and (d), as well as Figure 10 - 3(a) and (b). From the simulated electric field distribution presented in Figure 10 - 3(c) and (d), one could observe that the plane anode exhibited continuously high electric field along the anode surface (x -direction), while the hexagonal mesh exhibited alternate regions of both high and low electric field. The presence of low electric field regions could be attributed to the hexagonal openings present in the mesh,

which can result in lower electric field, thus corresponding to the lower FE current density in the CNT emitter.

Figure 10 - 3: Potential and electric field distribution on CNT emitters with (a) & (c) plane anode; and (b) & (d) hexagonal mesh, respectively

Apart from regular hexagon (RH) mesh, as illustrated in Figure 10 - 2, the FE performance induced by elongated hexagon (EH) mesh was compared as well. The schematic diagrams of both RH and EH meshes are as illustrated in Figure 10 - 4. As for the RH mesh, the hexagonal openings had equal sides (s and x), as displayed in Figure 10 - 4(a). Meanwhile, the EH mesh had elongated hexagonal opening along the x -direction (varied values of x), as shown in Figure 10 - 4(c). Moreover, in order to explore the varying geometrical combinations, 3 combinations of x and y values had been attempted, all the while keeping the length of the

slanted sides (s) fixed. As for the comparison between RH and EH meshes, the RH openings with $50\ \mu\text{m}$ sides (labelled as 'RH: $50\ \mu\text{m}$ ') had been applied. The geometrical descriptions on the investigated mesh with RH and EH designs are summarized in Table 10 - 1.

Figure 10 - 4: Plane view schematic diagrams of: RH mesh (a) Single RH opening, (b) CNT field emitter with RH mesh; EH mesh: (c) Single EH opening, (d) CNT field emitter with EH mesh (EH2)

Table 10 - 1: Mesh Label and Geometrical Specifications of RH and EH Meshes

Mesh Label	$s\ (\mu\text{m})$	$x\ (\mu\text{m})$	$y\ (\mu\text{m})$
RH: $50\ \mu\text{m}$	50	50	86.6
EH1	50	70	60
EH2	50	90	40
EH3	50	120	30

The simulated electric field distributions on CNT emitters with plane anode, RH mesh (RH:50 μm), and EH meshes are illustrated in Figure 10 - 5. In fact, Figure 10 - 5(a) shows that the hexagonal meshes induced lower electric field on CNT emitter, in comparison to that of plane anode. This could be attributed to the presence of low electric field regions in hexagonal openings, as displayed in Figure 10 - 3(d). In general, EH meshes induced higher electric field on CNT emitter, when compared to RH mesh. Among the EH meshes, the CNT field emitter with higher aspect ratio (x/y ratio) of hexagonal openings exhibited higher electric field. A possible cause for such scenario could be attributed to the electrostatic distribution nature upon elongated objects, where the field enhancement of hexagon structure increased with its aspect ratio [212], [213]. Furthermore, from the FN theory, higher field enhancement of an emitter can result in higher FE current density. Nevertheless, a possible drawback from the high electric field is the probable collision between the electrons in the mesh structure. As shown in the electron trajectories of CNT emitter with plane anode and hexagonal mesh (RH:50 μm) (Figure 10 - 6), a significant fraction of electrons that emitted from the CNT emitter hit on the mesh during the FE process. In precise, apart from the lower field enhancement by hexagonal mesh than plane anode, another trade-off that should be considered is the electron collision on mesh structure, which could reduce the number of electrons that enters the PH-SWS for signal gain.

Figure 10 - 5: Simulated electric field on CNT emitters with plane anode, RH mesh, and EH meshes: (a) along x-axis, (b) at $x = 0$

Figure 10 - 6: Electron trajectories of CNT field emitter with: (a) plane anode, and (b) hexagonal mesh (RH: 50 μm)

Based on the investigation pertaining to the effect of hexagonal mesh dimensions towards the current emitting behaviour of CNT field emitter, the FE current of CNT emitter with plane anode, RH mesh (RH:50 μm), and EH meshes had been simulated and as illustrated in Figure 10 - 7. With that, Figure 10 - 7(a) shows that the FE current of 45 mA was emitted from the CNT emitter with plane anode, similar to the FE measurements obtained in Figure 9 - 4(a). When the plane anode was substituted with a hexagonal mesh, the emitted current reduced due to the reduction in electric field, as discussed earlier. Similarly, the emitted current was found to increase gradually from RH: 50 μm to EH3 due to the shift in electric field enhancement on CNT surface. On top of that, despite of the higher emitted current, less electrons escaped from the EH meshes than RH:50 μm mesh, with a significant fraction of electrons found colliding on the EH meshes. Besides, as illustrated in Figure 10 - 7(a), as the mesh structure shifted from RH:50 μm to EH3 mesh, the percentage of electrons that collided on the mesh increased gradually. In addition, Figure 10 - 4 portrays that the EH meshes covered a larger area fraction of CNT emitter than RH:50 μm , thus causing more electrons to collide on the EH meshes. However, since the aim of this study is partially to minimize the number of

electrons colliding on the mesh structure, the RH mesh structure is preferred over the EH structure.

Figure 10 - 7: Current emitting behaviour of CNT field emitter with plane anode, RH mesh (RH: 50 μm), and EH meshes: (a) Current emitted from CNT emitter, and current escaped from mesh structure; (b) Percentage breakdown of electrons escaped from the mesh and collided on the mesh

So as to explore the possibilities in obtaining more electrons that escaped from the mesh structure, FE properties of CNT emitter with RH meshes of varying sizes had been investigated. RH meshes with 30, 50, 80, 100, and 150 μm sides, respectively, had been examined. Their respectively geometrical specifications and sample labelling are further tabulated in Table 10 - 2, while the schematic diagrams of RH meshes with varied sizes of hexagonal openings are illustrated in Figure 10 - 8. At larger RH sizes, lower electric field was obtained on CNT emitter,

as presented in Figure 10 - 9. This could be attributed to the presence of less hexagonal corners per unit area as the size of the hexagonal openings reduced. Furthermore, as depicted above, the sharp corners in the hexagonal mesh exhibited intensified electric field, which could possibly yield higher field enhancement on CNT emitter [211]. Moreover, as portrayed in Figure 10 - 8, for larger RH sizes, less RH corners were present per unit area on the mesh, hence resulting in lower electric field on the emitter. Another possibility for this trend is the area fraction of openings in meshes with larger RH sizes. As shown in Figure 10 - 3(d), the openings in hexagonal mesh generated low electric field regions, which reduced the overall field enhancement on CNT emitter. As for meshes with larger RH sizes, the higher area fraction of openings per unit area was present, which resulted in lower field on CNT emitter.

Figure 10 - 8: Schematic diagrams of RH meshes: (a) RH:30 μm , (b) RH:80 μm , (c) RH:100 μm , and (d) RH:150 μm

Table 10 - 2: Mesh Label and Geometrical Specifications of RH Meshes

Mesh Label	s, x (μm)
RH: 30 μm	30
RH: 50 μm	50
RH: 80 μm	80
RH: 100 μm	100
RH: 150 μm	150

Figure 10 - 9: Simulated electric field on CNT emitters with plane anode and RH meshes: (a) along x -axis, and (b) at $x = 0$

Figure 10 - 10 displays the simulated FE current from CNT emitter with RH meshes of varying sizes. Based on Figure 10 - 10(a), the emitted current was found to reduce with the increasing RH sizes. This is attributed to the reduced electric field on CNT emitter with the increasing RH sizes, as discussed earlier. In addition, it was observed that more electrons escaped from the hexagonal mesh at larger RH openings, primarily due to less emitter area covered by the mesh structure. This can be observed in the schematic diagrams of RH meshes illustrated in Figure 10 - 8. Although the emitter with RH:100 μm mesh emitted slightly higher current than that of the RH:150 μm mesh emitter, the RH:150 μm caused less collision among

the electrons on the mesh structure, with lower percentage of electrons hitting on the mesh, as compared to RH: 100 μm , which can be noted in Figure 10 - 10(b). Besides, in line with the aim to minimize collision between the electrons on the hexagonal mesh, the RH:150 μm was selected as the most preferred mesh design among those investigated.

Figure 10 - 10: Current emitting behaviour of CNT field emitter with plane anode and RH meshes: (a) Current emitted from CNT emitter, and current escaped from mesh structure; (b) Percentage breakdown of electrons escaped from the mesh and collided on the mesh

From the obtained simulation results, CNT emitter with RH:150 μm mesh exhibited the most desirable FE behaviour. FE current of ~20 mA had been speculated to escape from the mesh structure, with minimal electron collision on the mesh. Hence, such FE condition had been applied to further look into the feasibility of applying such CNT emitter in PH-SWS TWTA.

10.3 Integration of Screen-Printed Carbon Nanotubes (CNTs) Field Emitter in Planar Helix-Slow Wave Structure Traveling Wave Tube Amplifier (PH-SWS TWTA)

As described in Chapter 4, (Figure 4 - 1(c) and Table 4 - 1), the cross-sectional dimension of PH-SWS had been fixed at $300 \times 700 \mu\text{m}$ for Ka-band operation. Meanwhile, the smallest cathode area of screen-printed CNT field emitters, as reported in Chapter 9 that is $0.5 \times 1 \text{ mm}$, had been found to cause electron collision on PH-SWS if integrated directly into the TWTA. Therefore, in order to address this issue, a beam-forming electrode (BFE) was used to ‘compress’ the electron beam into smaller beam waist, yet retaining the required beam current for signal amplification [15]. The schematic diagram of the BFE is as shown in Figure 10 - 11(a), while the details of the BFE-cathode assembly is as described in a reported prior study [15]. Since 5 kV electron beam voltage had been required for Ka-Band operation (as indicated in Table 4 - 2), the TWTA voltage was fixed at 5000 V. The voltage distribution on TWTA and BFE is portrayed in Figure 10 - 11(b).

Figure 10 - 11: (a) Schematic diagram of BFE, (b) Potential Distribution, (c) Electron Trajectory, and (d) Electric field distribution in BFE and TWTA

Figure 10 - 11 (c) and (d) portray the electron trajectory and the electric field distribution in both BFE and TWTA. Meanwhile, Figure 10 - 11(c) displays the converged electron beam from $0.5 \times 1 \text{ mm}$ to $60 \times 200 \mu\text{m}$. The convergence of electrons could be attributed to the presence of negative field region induced by BFE, as shown in Figure 10 - 11(d). Beyond the beam waist position, the focusing magnetic field began restricting the spread of electron. Furthermore, by using the obtained $60 \times 200 \mu\text{m}$ beam waist with 20 mA emission current, PIC simulation on PH-SWS TWT had been conducted, where other parameters had been fixed, as summarized in Chapter 4.

Figure 10 - 12: (a) Input and output signals of PH-SWS TWT, (b) elliptical cross-section of the electron beam, under 20 mA electron beam, $60 \times 200 \mu\text{m}$ rectangular electron emitter

Figure 10 - 12(a) illustrates both input and output power of PH-SWS TWT amplified by electron beam of 20 mA current with $60 \times 200 \mu\text{m}$ cross-sectional dimension. The signal gain of ~ 28 dB had been calculated. Interestingly, at 20 mA beam current and $60 \times 200 \mu\text{m}$ emitter dimension, no electron collision occurred on the PH-SWS. This differed from the PIC results depicted in Chapter 4 (Figure 4 - 3), where electron collision occurred at 20 mA. The reason for this is the convergence of electron beam by BFE, which compressed the electron beam into $60 \times 200 \mu\text{m}$ cross-sectional dimension. As this compressed dimension is smaller than the $150 \times 350 \mu\text{m}$ rectangular emitter assumed in Chapter 4, it is possible that smaller electron emission area can result in narrower electron beam, hence enabling it to fit into the PH-SWS tunnel. Nevertheless, in the actual application of CNT field emitter, the applied voltage can be reduced to obtain lower FE current with narrower beam current [114]. This suggests more tolerance to fit the electron beam into PH-SWS, which offers higher feasibility in the actual integration of CNT emitter into PH-SWS TWTA.

10.4 Summary

CNT field emitters were synthesized by using the screen-printing technique. With that, the FE current density of 9 A/cm^2 had been achieved consistently by using the $0.5 \times 1 \text{ mm}$ rectangular CNT emitter. By using the optimum FE current density; the design and the simulation of hexagonal mesh had been carried out. An idealized mesh design with minimized electron collision on the mesh structure was selected. From the selected design, 20 mA current emission was emitted, thus yielding ~28 dB signal gain in PH-SWS TWTA. This fulfils the objective of this thesis, in which the CNT field emitter had been designed, simulated, and synthesized so as to obtain signal gain of $> 20 \text{ dB}$ in PH-SWS TWTA.

10.5 Publication

Y. D. Lim, J.T. Chen, C.B. Yan *et al.* “Hexagonal Mesh Screen-Printed Carbon Nanotubes Field Emitter for Microfabricated Traveling Wave Tube”, *IEEE Transactions on Electron Devices* - **Submitted**

Chapter 11: Thesis Summary and Recommendations for Future Work

11.1 Thesis Summary

The main objective of this PhD thesis is to design and to fabricate a Carbon Nanotubes (CNT) field emitter that is capable of inducing > 20 dB signal gain in PH-SWS TWTA under Ka-Band operation. In order to achieve this particular objective, several research approaches had been investigated, including: determining the required electron emission condition for > 20 dB signal gain in PH-SWS TWTA, selection of the most suitable CNT growth technique for high FE performance, design and fabrication of CNT field emitter, as well as simulation of signal gain performance in PH-SWS TWTA using the obtained FE performance from the CNT field emitter.

In order to determine the electron emission condition that is required to achieve > 20 dB signal gain in PH-SWS TWTA under Ka-Band frequency, the signal gain of PH-SWS TWTA under varying electron beam current had been simulated. At higher electron beam current, higher signal gain was found in PH-SWS TWTA, but the electron beam exhibited more stringent rotational tolerance in the PH-SWS. Thus, in order to obtain signal gain of > 20 dB, the electron beam current of 10 mA had been required. Under $\sim 0.75 \text{ mm}^2$ cathode area, 10 mA electron beam current corresponded to FE current density of $\sim 1.5 \text{ A/cm}^2$. The details of the PH-SWS TWTA simulation are reported in Chapter 4.

Next, in the attempt to determine the most favourable growth technique of current-emitting CNTs to attain high FE current density, various Chemical Vapour Deposition (CVD) techniques were performed. The FE properties of CNTs grown using Plasma-Enhanced Chemical Vapour Deposition (PECVD), floating catalyst Thermal Chemical Vapour

Deposition (TCVD), and pre-deposited TCVD techniques were investigated. Under similar CNT height of 10 ~ 11 μm , the floating catalyst TCVD-grown CNTs displayed exceptional FE current density of 1.43 mA/cm^2 under 7 $\text{V}/\mu\text{m}$ applied electric field, in comparison to pre-deposited catalyst TCVD CNTs (1.17 mA/cm^2 @ 7 $\text{V}/\mu\text{m}$) and PECVD-grown CNTs (0.6 mA/cm^2 @ 7 $\text{V}/\mu\text{m}$). In fact, the outstanding FE current density could be attributed to the higher field enhancement on CNT tips, primarily due to the small CNT diameter (high CNT aspect ratio) and enlarged CNT tips. The details of the FE properties of various CNTs are reported in Chapters 5 and 6.

Next, to fabricate the CNT field emitter for high FE current density using the floating catalyst TCVD technique, the CNTs, first, were grown selectively on the Si surfaces of the Si/SiO₂ structure. By investigating the CNT growth on both Si and SiO₂ surfaces under 760 – 880 °C growth temperatures, selective CNT growth on Si surface was gained under 790 °C growth temperature. Besides, several isolated CNT bundles were grown selectively on the Si surfaces to obtain FE current density of 76.9 mA/cm^2 under 49.7 $\text{V}/\mu\text{m}$ applied electric field. Moreover, upon confinement of CNT bundles in 0.5 μm diameter SiO₂ pits, improved FE current density of 1 – 1.4 A/cm^2 had been generated due to the higher field enhancement in CNT bundles. The details of the selective growth of CNTs on Si surfaces are reported in Chapter 7, while the FE properties of CNT bundles confined in SiO₂ pits are elaborated in Chapter 8.

To further explore the enhancement in FE current density, the FE properties of screen-printed CNTs had been determined. As such, ~5 nm diameter single-walled CNTs had been mixed with nanoparticles additives and Ethyl Cellulose adhesive to form CNT paste, which was later printed onto the Si substrates. High FE current density of 9 A/cm^2 was obtained consistently from 0.5×1 mm screen-printed cathode. By using the obtained FE condition, a hexagonal mesh was designed and simulated to obtain the optimized mesh design. Under the

optimized hexagonal mesh, the FE current emitted from the mesh was simulated. As a result, some 20 mA current could be expected to emit from the optimized hexagonal mesh, which corresponds to ~28 dB signal gain in PH-SWS TWTA. This eventually has fulfilled the objective outlined in this PhD thesis, which is to design and to fabricate a CNT field emitter that is capable of inducing > 20 dB signal gain in PH-SWS TWTA.

11.2 Recommendations for Future Work

Based on the findings and discussion presented in the thesis, the following suggestions are made to further explore the research topic:

11.2.1 Optimization of Screen-Printed Carbon Nanotubes (CNTs) Field Emitter

Based on Chapter 9, it had been pointed out that screen-printed CNTs do exhibit excellent FE current density, so as much achieving 9 A/cm² consistently under repeated measurement. The excellent FE properties can be attributed to the mixture of nanoparticles additives and ethyl cellulose adhesive, which had been proven to improve both the electrical properties and the substrate adhesion of CNTs, respectively. Moreover, it is highly possible that the weight composition ratio of nanoparticles/ethyl cellulose/CNTs plays a major role in the resulting FE properties. Therefore, the recipe of the weight composition ratio (mass of Ni, ITO particles, etc.) can be varied and optimized, so as to explore further improvement in its corresponding FE properties. Besides, it has also been reported that the addition of Ruthenium (Ru) can improve the FE properties of CNTs [214], in which the effect of Ru particles decoration on the CNT FE properties can be compared with that of Ni and ITO particles. Apart from the particles decoration, the substrate of which CNTs are printed can be speculated to exert a significant impact upon the CNTs' substrate adhesion, where the usage of high conductivity metallic substrate (Ni for instance [100]) can possibly offer further enhancement to its corresponding FE properties.

11.2.2 Optimization of Mesh Structure for Screen-Printed Carbon Nanotubes (CNTs)

Field Emitter

From Chapter 10, a hexagonal mesh was designed and optimized to obtain maximum number of electrons escaping from the mesh, yet minimal electron collision onto the mesh itself. Hexagonal mesh was chosen as the sole design due to the presence of corners in the hexagonal shape, which can exert high electric field onto the surface of the screen-printed CNTs. Since the presence of corners exerts high electric field onto CNTs, it is also possible that mesh openings with other shapes, such as heptagonal or octagonal shapes, can induce high field enhancement onto the surface of the emitter. Nevertheless, to a certain extent when there are too many corners in a single opening, the opening may exhibit spherical-like electric field distribution, which could impair its overall electric field enhancement on the emitter surface. Hence, it is necessary to compare the electric field distribution in mesh openings of various shapes (pentagonal, hexagonal, heptagonal, etc.) to obtain more desirable FE behaviour from the screen-printed CNT field emitter.

11.2.3 Fabrication and Field Emission (FE) Characterization CNT Field Emitter

Integrated with Mesh

After obtaining the optimized recipe for screen-printed CNT field emitter depicted in Section 11.2.1 and optimized mesh design elaborated in Section 11.2.2, a CNT field emitter with mesh can be fabricated successfully. The schematic diagram of the fabrication and the assembly for CNT field emitter with mesh are illustrated in Figure 11 - 1. In fact, 300 μm thick mica spacer can be used as the spacer between the CNT field emitter and the mesh, which reflects the actual FE measurement condition. As for the mesh, it can be fabricated by means of photolithography patterning on highly-doped Si wafer to obtain the desired pattern, and followed by Deep Reactive Ion Etching (DRIE) to etch through the wafer. Meanwhile, as for the FE characterization, the current measurement can be applied on the CNT field emitter and

the mesh structure to determine the actual current emitted from the emitter, collided on the mesh, and escaped from the mesh into the PH-SWS.

Figure 11 - 1: Schematic diagram of: (a) Screen-printed CNTs and mica spacer assembly, and (b) assembly of fabricated mesh with mica spacer and screen-printed CNTs

11.2.4 Long-term Reliability of the Screen-Printed CNT Field Emitter with Mesh

Structure

From the repeated FE measurement on the screen-printed CNTs, as presented in Chapter 9 (Figure 9 - 5), the CNTs exhibited consistent and recurring FE characteristics regardless of the cathode area and the dimension (0.5×1, 1×2, and 2×4 mm). This reflects a satisfactory level of emission stability by the printed CNTs. Thus, in order to further justify the emission stability, long-term emission stability test of a few hours to a few days can be carried out on the printed CNTs. Besides, in order to enhance the technological readiness of the CNT

field emitter, the possible heat-induced damages on the mesh caused by electron collision can also be identified, investigated, and addressed.

Author's Publications

Journal Papers

Lim Y D, Hu L, Vasiliyovich A, Grapov D, Tay B K, Aditya S, Miao J and Labunov V 2017 Temperature-dependent selective growth of carbon nanotubes in Si / SiO₂ structures for field emitter array applications *Materials Research Bulletin* 95 129–37

Lim Y D, Avramchuck A V, Grapov D, Tan C W, Tay B K, Aditya S and Labunov V 2017 Enhanced Carbon Nanotubes Growth Using Nickel/Ferrocene-Hybridized Catalyst *ACS Omega* 2 6063–71

Lim Y D, Hu L, Xia X, Syed Mohammed Z A, Wang S, Tay B K, Aditya S and Miao J 2017 Field Emission Properties of SiO₂-wrapped CNT Field Emitter *Nanotechnology* 29 15202

Lim Y D, Kong Q, Wang S, Tan C W, Tay B K and Aditya S 2017 Enhanced field emission properties of carbon nanotube films using densification technique *Appl. Surf. Sci.* In Press

Lim Y D, Grapov D, Hu L, Kong Q, Tay B K, Labunov V, Miao J, Coquet P, Aditya S 2017 Enhanced Field Emission Properties of Carbon Nanotube Bundles Confined in SiO₂ pits *Nanotechnology* – Accepted

Lim Y D, Kong Q, Tan C W, Liang K, Tay B K, Aditya, S 2017 Field Emission Properties of Three-Dimensional Carbon Nanotubes Network *Materials Research Express* – Under review

Lim Y D, Chen J T, Yan X B, Liang K, Wang S, Aditya S, Tay B K 2017 Hexagonal Mesh Screen-printed Carbon Nanotubes Field Emitter for Microfabricated Traveling Wave Tube *IEEE Transactions on Electron Devices* – Under review

Lim Y D, Grapov D, Xia X, Hu L, Wang S, Tay B K, Aditya S, Labunov V, Miao J 2017 Design and Fabrication of Carbon Nanotubes Field Emitter for Microfabricated Traveling-Wave Tube *IEEE Transactions on Nanotechnology* – Under review

References

Conference

Lim Y D, Avramchuck A, Grapov D, Tay B K, Aditya S, Labunov V “*Field Emission Characteristics of Short CNT Bundles*” IEEE International Vacuum Electronics Conference 2016, Monterey, USA

Lim Y D, Kong Q, Tay B K, Aditya S “*Enhanced Field Emission Characteristics of Carbon Nanotube Films via Surface Modification Technique*” Surfcoat Korea 2017, Incheon, Korea

Lim Y D, Wang S, Aditya S, Tay B K, Labunov V “*Computational Exploration on the Application of Carbon Nanotubes in Planar Helix Slow-Wave Structure Traveling Wave Tubes*” Nanomeeting 2017, Minsk, Belarus

Lim Y D, Grapov D, Wang S, Tay B K, Aditya, S, Labunov V “*Field Emission Properties of Ex-situ and In-situ Iron Catalyst-Grown Carbon Nanotubes*” IEEE Nanotechnology Materials and Devices Conference 2017, Singapore

Lim Y D, Wang S, Tay B K, Aditya, S “*Simulated Behavior of Planar-Helix Slow-Wave Structure Traveling-Wave Tube at Various Electron Beam Current*” IEEE Nanotechnology Materials and Devices Conference 2017, Singapore

References

- [1] A. Schnapf, “TIROS-N - THE OPERATIONAL ENVIRONMENTAL SATELLITE OF THE 80’S,” in *AIAA Commun Satell Syst Conf*, 1980.
- [2] H. M. Jones;, I. I. Shapiro;, and P. E. Zadunaisky, “Solar Radiation Pressure Effects, Gas Leakage Rates, and Air Densities Inferred From the Orbit Of Echo I,” in *Second International Space Science Symposium*, 1961.
- [3] J. F. DONNELLY, G. RP, and K. JD, “DESIGN OF MECHANICALLY DESPUN

References

- ANTENNA FOR INTELSAT-III COMMUNICATIONS SATELLITE,” *IEEE Trans. Antennas Propag.*, vol. 17, no. 4, pp. 407–415, 1969.
- [4] Spacefacts, “An Early History of Satellites! 1950-1978.” [Online]. Available: <http://www.jpl.nasa.gov/infographics/infographic.view.php?id=11182>. [Accessed: 14-May-2015].
- [5] B. Lewis, “Ka-band vs. Ku-band: the Knowledge You Need to Make the Right Decision for Your Organization,” 2013. [Online]. Available: <http://www.intelsat.com/blog/ka-band-vs-ku-band-the-knowledge-you-need-to-make-the-right-decision-for-your-organization/>. [Accessed: 20-May-2015].
- [6] SpaceWorks, “Nano/Microsatellite Market Assessment,” *SpaceWorks*, 2014. [Online]. Available: http://www.sei.aero/eng/papers/uploads/archive/SpaceWorks_Nano_Microsatellite_Market_Assessment_January_2014.pdf. [Accessed: 14-May-2015].
- [7] D. Bishop, “Nanotechnology and the end of Moore’s Law?,” *Bell Syst. Tech. J.*, vol. 10, no. 3, pp. 23–28, 2005.
- [8] H. Iwai, “End of the scaling theory and Moore’s law,” *2016 16th Int. Work. Junction Technol.*, pp. 1–4, 2016.
- [9] J. Han and M. Meyyappan, “The device made of nothing,” *IEEE Spectr.*, vol. 51, no. 7, pp. 30–35, Jul. 2014.
- [10] A. S. Gilmour, *Klystrons, Traveling Wave Tubes, Magnetrons, Crossed-Field Amplifiers, and Gyrotrons*. Artech House, 2011.
- [11] W. L. Menninger, S. Aldana-Gutierrez, R. T. Benton, X. Zhai, D. Zamora, and W. L. McGeary, “High-efficiency, qualification-tested, 50-130-W k-band traveling-wave

References

- tubes for satellite communications downlinks,” *IEEE Int. Vac. Electron. Conf.*, pp. 1–2, 2015.
- [12] J. X. Qiu *et al.*, “Vacuum tube amplifiers,” *IEEE Microw. Mag.*, vol. 10, no. 7, pp. 38–51, 2009.
- [13] K. Swaminathan, C. Zhao, C. Chua, and S. Aditya, “Vane-loaded planar helix slow-wave structure for application in broadband traveling-wave tubes,” *IEEE Trans. Electron Devices*, vol. 62, no. 3, pp. 1017–1023, 2015.
- [14] S. Wang, C. Zhao, and S. Aditya, “Design of a Sheet-Beam Electron Gun for a Ka-Band Microfabricated Traveling-Wave Tube,” *IEEE Int. Vac. Electron. Conf.*, 2015.
- [15] S. Wang, S. Aditya, and S. Member, “Design of a Sheet-Beam Electron-Optical System for a Microfabricated W -Band Traveling-Wave Tube Using a Cold Cathode,” *IEEE Trans. Electron Devices*, vol. 63, no. 9, pp. 3725–3732, 2016.
- [16] K. Panda, K. J. Sankaran, B. K. Panigrahi, N. H. Tai, and I. N. Lin, “Direct observation and mechanism for enhanced electron emission in hydrogen plasma-treated diamond nanowire films,” *ACS Appl. Mater. Interfaces*, vol. 6, no. 11, pp. 8531–8541, 2014.
- [17] Y. Zhang, C. Wu, Y. Zheng, and T. Guo, “Synthesis and efficient field emission characteristics of patterned ZnO nanowires,” *J. Semicond.*, vol. 33, no. 2, p. 23001, 2012.
- [18] A. K. Samantara *et al.*, “Facile synthesis of Ag nanowire-rGO composites and their promising field emission performance,” *RSC Adv.*, vol. 5, no. 52, pp. 41887–41893, 2015.
- [19] W. I. Milne *et al.*, “Carbon nanotubes as field emission sources,” *J. Mater. Chem.*, vol.

References

- 14, no. 6, p. 933, 2004.
- [20] C. Liu, Y. Zheng, G. Ding, J. Wu, and F. Zang, “Numerical analysis in field emission characteristics of carbon nanotube field emitters and arrays,” in *Proceedings of the Institution of Mechanical Engineers, Part N: Journal of Nanoengineering and Nanosystems*, 2012, vol. 227, no. 1, pp. 39–45.
- [21] H. S. Uh, S. Park, and B. Kim, “Enhanced field emission properties from titanium-coated carbon nanotubes,” *Diam. Relat. Mater.*, vol. 19, no. 5–6, pp. 586–589, 2010.
- [22] BRYCE Space and Technology, “State of the Satellite Industry Report,” 2017.
- [23] S. M. & Research, “Satellite TV Revenues to Overtake Cable in 2015,” 2014.
[Online]. Available: <http://satellitemarkets.com/market-trends/satellite-tv-revenues-overtake-cable-2015>. [Accessed: 20-May-2015].
- [24] R. Sandau, L. Paxton, and J. Esper, “Trends and Visions for Small Satellite Missions,” in *Small Satellites for Earth Observation*, 2008, pp. 27–39.
- [25] R. Sandau, K. Brieß, and M. D’Errico, “Small satellites for global coverage: Potential and limits,” *ISPRS J. Photogramm. Remote Sens.*, vol. 65, no. 6, pp. 492–504, 2010.
- [26] SpaceWorks Enterprises, “2017 Nano/Microsatellite Market Forecast,” 2017.
- [27] R. Thom Stone, “Introduction to Satellite Communications Technology for Nren,” California, 2004.
- [28] K. Seifu and D. Law, “Communication Satellites: Frequency Band limitations Versus Implementations.”
- [29] I. Objects, “Technical Challenges of Wireless Communications,” 2011.
- [30] ESA, “Satellite Frequency Bands,” 2013. [Online]. Available:

References

- http://www.esa.int/Our_Activities/Telecommunications_Integrated_Applications/Satellite_frequency_bands. [Accessed: 18-May-2015].
- [31] N. S. (NASA G. R. C. KilKenny, “Ka-Band Represents the Future of Space Communications,” 2015. [Online]. Available: https://www.nasa.gov/mission_pages/station/research/news/ka_band. [Accessed: 18-May-2015].
- [32] K. Palem and A. Lingamneni, “What to Do About the End of Moore’s Law, Probably!,” *Dac 2012*, pp. 1–6, 2012.
- [33] P. a. Redhead, “Vacuum and the electron tube industry,” *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 23, no. 4, p. 1252, 2005.
- [34] F. Guthrie, “On a relation between heat and static electricity,” *London, Edinburgh Dublin Philos. Mag. J. Sci.*, vol. 46, no. 4, pp. 257–266, 1873.
- [35] R. G. Arns, “The other transistor: early history of the metal-oxide semiconductor field-effect transistor,” *Eng. Sci. Educ. J.*, vol. 7, no. 5, p. 233, 1998.
- [36] G. Gaertner, “Historical development and future trends of vacuum electronics,” *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, vol. 30, no. 6, p. 60801, 2012.
- [37] B. Coaker and T. Challis, “Travelling wave tubes: Modern devices and contemporary applications,” *Microw. J.*, vol. 51, no. 10, pp. 32–46, 2008.
- [38] J. H. B. & R. J. Barker, “Introduction and overview,” in *Modern Microwave and Millimeter-Wave Power Electronics*, 2003, pp. 1–33.
- [39] J. H. Booske *et al.*, “Vacuum electronic high power terahertz sources,” *IEEE Trans. Terahertz Sci. Technol.*, vol. 1, no. 1, pp. 54–75, 2011.

References

- [40] R. S. Symons, “Modern microwave power sources,” *IEEE Aerosp. Electron. Syst. Mag.*, vol. 17, no. 1, pp. 19–26, 2002.
- [41] D. Murdock and M. C. Woods, “GaN Thermal Analysis for High-Performance Systems,” 2014.
- [42] D. Fox, “Gallium Nitride : The Superman of Semiconductors.” [Online]. Available: http://www.arts.cornell.edu/knight_institute/publicationsprizes/discoveries/discoveries_spring2014/03_Fox.pdf. [Accessed: 05-Dec-2015].
- [43] G. Hemts, Y. Wu, and P. Parikh, “High-power GaN HEMTs battle for vacuum-tube territory,” *Compd. Semicond.*, no. February, 2006.
- [44] C. M. Armstrong, “The Vitality of Vacuum Electronics,” no. 650, pp. 2–4.
- [45] S. Okazaki, “High resolution optical lithography or high throughput electron beam lithography: The technical struggle from the micro to the nano-fabrication evolution,” *Microelectron. Eng.*, vol. 133, pp. 23–35, 2015.
- [46] P. Atkins and L. Jones, *Chemistry. Molecules, Matter and Change*, 3rd ed. New York: W.H. Freeman, 1997.
- [47] R. R. Tummala, *Fundamentals of Microsystems Packaging*. Atlanta: McGraw-Hill, 2004.
- [48] A. Bar-Cohen, A. Watwe, and N. Seetharamu, Kankanhally, “Fundamentals of Thermal Management,” in *Fundamentals of Microsystem Packaging*, Atlanta: McGraw-Hill, 2004, pp. 215–266.
- [49] W. Lohmeyer and K. Cahoy, “Space weather radiation effects on geostationary satellite solid-state power amplifiers,” *AGU Sp. Weather*, vol. 11, pp. 476–488, 2013.

References

- [50] E. Illokken, "TWT Reliability in Space," *Aerosp. Electron. Syst. Mag.*, vol. 2, no. 7, pp. 22–24, 1987.
- [51] W. Q. Lohmeyer, R. J. Aniceto, and K. L. Cahoy, "Communication satellite power amplifiers: current and future SSPA and TWTA technologies," *Int. J. Satell. Commun. Netw.*, vol. In press, 2015.
- [52] G. Caryotakis, "Klystrons," in *Modern Microwave and Millimeter-Wave Power Electronics*, Wiley-IEEE Press, 2005, pp. 107–170.
- [53] J. H. Booske, D. R. Whaley, W. L. Menninger, R. S. Hollister, and C. M. Armstrong, "TRAVELING-WAVE TUBES," in *Modern Microwave and Millimeter-Wave Power Electronics*, 2003, pp. 171–245.
- [54] R. Kompfner, "Travelling-wave tubes," *Reports Prog. Phys.*, vol. 275, 1952.
- [55] H. H. Song, "Calculation of Start-Oscillation-Current for Lossy Gyrotron Traveling-Wave Tube (Gyro-TWT) Using Linear Traveling-Wave Tube (TWT) Parameter Conversions," *J. Electromagn. Anal. Appl.*, vol. 5, no. 1, pp. 1–4, 2013.
- [56] E. J. Kowalski, M. A. Shapiro, and R. J. Temkin, "An Overmoded W-Band Coupled-Cavity TWT," *IEEE Trans. Electron Devices*, vol. 62, no. 5, pp. 1609–1616, 2015.
- [57] Z. S. & L. W. C, Chua, J.M. Tsai, S. Aditya, M. Tang, S.W. Ho, "Microfabrication and Characterization of W-Band Planar Helix Slow-Wave Structure With Straight-Edge Connections," *IEEE Trans. Electron Devices*, vol. 58, no. 11, pp. 4098–4105, 2011.
- [58] L. Communications, "Mini Traveling Wave Tubes," 2015. [Online]. Available: http://www2.1-3com.com/edd/pdfs/minitwts_06all.pdf. [Accessed: 06-Jun-2015].
- [59] P. a. Redhead, "The birth of electronics: Thermionic emission and vacuum," *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 16, no. 3, p. 1394, 1998.

References

- [60] M. N. Avadhanulu and P. G. Kshirsagar, *A Textbook for Engineering Physics*. S. Chand, 1992.
- [61] S. Yamamoto, “Fundamental physics of vacuum electron sources,” *Reports Prog. Phys.*, vol. 69, no. 1, pp. 181–232, 2005.
- [62] J.-H. Lee, B. K. Vancil, T. O. Gwinn, R. Maboudian, N. A. Melosh, and R. T. Howe, “Microfabricated Thermally Isolated Low Work-Function Emitter,” *J. Microelectromechanical Syst.*, vol. 23, no. 5, pp. 1182–1187, 2014.
- [63] L. Dong *et al.*, “Fabrication and thermionic emission properties of lanthanum carbide doped tungsten cathodes,” *Mater. Lett.*, vol. 146, pp. 47–50, 2015.
- [64] D. Codron, K. Goodfellow, and D. Erwin, “Thorium Migrational Effects on Cathode Temperature in Electric Thrusters,” *J. Propuls. Power*, vol. 29, no. 1, pp. 158–165, 2013.
- [65] P. Sarrazin *et al.*, “Carbon-Nanotube Field Emission X-Ray Tube for Space Exploration Xrd / Xrf Instrument .,” *Int. Cent. Diffraction Data*, vol. 47, pp. 232–239, 2004.
- [66] P. Schagen, “Alternatives to thermionic emission,” *Br. J. Appl. Phys.*, vol. 16, no. 3, pp. 293–303, 1965.
- [67] R. H. Fowler and L. Nordheim, “Electron Emission in Intense Electric Fields,” in *Proceedings of the Royal Society*, 1928, vol. 119, pp. 173–181.
- [68] R. C. Smith, D. C. Cox, and S. R. P. Silva, “Electron field emission from a single carbon nanotube: Effects of anode location,” *Appl. Phys. Lett.*, vol. 87, no. 10, pp. 131–133, 2005.
- [69] C. a. Spindt, C. M. Armstrong, C. R. Smith, B. M. Gannon, and D. R. Whaley, “Application of field emitter arrays to microwave power amplifiers,” *IEEE Trans.*

References

- Plasma Sci.*, vol. 28, no. 3, pp. 727–747, 2000.
- [70] C. a. Spindt, “A thin-film field-emission cathode,” *J. Appl. Phys.*, vol. 39, no. 7, pp. 3504–3505, 1968.
- [71] C. A. Spindt, K. R. Shoulders, and L. N. Heynick, “Field Emission Cathode Structures and Devices Utilizing such Structures,” 3755704, 1973.
- [72] V. M. Aguero and R. C. Adamo, “Space Applications of Spindt Cathode Field Emission Arrays,” *6th Spacecr. Charg. Technol. Conf.*, no. September, pp. 347–352, 2000.
- [73] X. Li, G. Bai, H. Li, M. Ding, J. Feng, and F. Liao, “A Potential Failure Reason for Spindt Cathodes in High Current Applications,” pp. 509–510, 2014.
- [74] T. Utsumi, “Vacuum microelectronics: what’s new and exciting,” *IEEE Trans. Electron Devices*, vol. 38, no. 10, pp. 2276–2283, 1991.
- [75] G. Mittal and I. Lahiri, “Recent progress in nanostructured next-generation field emission devices,” *J. Phys. D. Appl. Phys.*, vol. 47, no. 32, p. 323001, Aug. 2014.
- [76] F. Jamali Sheini, D. S. Joag, M. a. More, J. Singh, and O. N. Srivasatva, “Low temperature growth of aligned ZnO nanowires and their application as field emission cathodes,” *Mater. Chem. Phys.*, vol. 120, no. 2–3, pp. 691–696, 2010.
- [77] S. Garry, É. McCarthy, J.-P. Mosnier, and E. McGlynn, “Influence of ZnO nanowire array morphology on field emission characteristics,” *Nanotechnology*, vol. 25, no. 13, p. 135604, 2014.
- [78] C. Jiang, S. Liu, X. Chen, and S. Yu, “Controllable growth of a forest of silver nanowires and their field emission properties,” *CrystEngComm*, vol. 16, no. 37, p. 8646, 2014.

References

- [79] C. Wu, F. Li, Y. Zhang, and T. Guo, "Field emission from vertical graphene sheets formed by screen-printing technique," *Vacuum*, vol. 94, pp. 48–52, 2013.
- [80] K. H. Park, S. Lee, and K. H. Koh, "High current field emission behavior of carbon nanofiber film: Adsorbate effects," *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, vol. 24, no. 3, p. 1353, 2006.
- [81] a. L. Musatov, K. R. Izrael'yants, a. B. Ormont, E. G. Chirkova, and E. F. Kukovitsky, "High Current Density Planar Field Electron Emitters with Carbon Nanotubes," *Fullerenes, Nanotub. Carbon Nanostructures*, vol. 19, no. 1–2, pp. 100–104, Nov. 2010.
- [82] Z.-S. Wu *et al.*, "Field Emission of Single-Layer Graphene Films Prepared by Electrophoretic Deposition," *Adv. Mater.*, vol. 21, no. 17, pp. 1756–1760, 2009.
- [83] H. S. Sim *et al.*, "Field emission from a single carbon nanofiber at sub 100 nm gap," *Appl. Phys. Lett.*, vol. 93, no. 2, pp. 0–3, 2008.
- [84] Y. Saito, "Structures and Synthesis of Carbon Nanotubes," in *Carbon Nanotube and Related Field Emitters: Fundamentals and Applications*, Weinheim: WILEY-VCH, 2010, pp. 3–14.
- [85] W. A. de Heer and A. Chatelain, "A carbon nanotube field-emission electron source," *Science (80-.)*, vol. 270, no. 5239, pp. 1179–1181, 1995.
- [86] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, pp. 56–58, 1991.
- [87] M. Monthieux, "Introduction to Carbon Nanotubes," in *Carbon Meta-Nanotubes: Synthesis, Properties and Applications*², 1st ed., M. Monthieux, Ed. John Wiley & Sons, Ltd, 2012, pp. 47–118.

References

- [88] L. Ci, J. Wei, B. Wei, J. Liang, C. Xu, and D. Wu, “Carbon nanofibers and single-walled carbon nanotubes prepared by the floating catalyst method,” *Carbon N. Y.*, vol. 39, no. 3, pp. 329–335, 2001.
- [89] J.-P. Bourgoïn, A. Loiseau, and J.-F. Nierengarten, “Fullerenes and Carbon Nanotubes,” in *Nanoscience*, Springer Berlin Heidelberg, 2007, pp. 279–323.
- [90] M. Monthieux *et al.*, “Introduction to Carbon Nanotubes,” in *Nanotechnology Handbook*, 3rd ed., Heidelberg: Springer Verlag, 2010, pp. 47–118.
- [91] N. Jonge and J.-M. Bonard, “Carbon nanotube electron sources and applications,” *Philos. Transactions R. Soc. London*, vol. 362, pp. 2239–2266, 2004.
- [92] S. D. Liang and L. Chen, “Theory of field and thermionic electron emissions of carbon nanotubes,” *Tech. Dig. - 2009 22nd Int. Vac. Nanoelectron. Conf. IVNC 2009*, pp. 101–102, 2009.
- [93] S. Han, “Field Emission Theory,” in *Carbon Nanotube and Related Field Emitters: Fundamentals and Applications*, Weinheim: WILEY-VCH, 2010, pp. 43–54.
- [94] G. Bocharov and A. Eletsii, “Theory of Carbon Nanotube (CNT)-Based Electron Field Emitters,” *Nanomaterials*, vol. 3, no. 3, pp. 393–442, 2013.
- [95] K. Watanabe and M. Araidai, “Field Emission from Graphitic Nanostructures,” in *Carbon Nanotube and Related Field Emitters: Fundamentals and Applications*, Weinheim: WILEY-VCH, 2010, pp. 55–66.
- [96] J. S. Suh, K. S. Jeong, J. S. Lee, and I. Han, “Study of the field-screening effect of highly ordered carbon nanotube arrays,” *Appl. Phys. Lett.*, vol. 80, no. 13, pp. 2392–2394, 2002.
- [97] H. Murata and H. Shimoyama, “Simulated Electric Field in an Array of CNTs,” in

References

- Carbon Nanotube and Related Field Emitters: Fundamentals and Applications*,
Weinheim: WILEY-VCH, 2010, pp. 143–162.
- [98] M. Kumar and Y. Ando, “Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production.,” *J. Nanosci. Nanotechnol.*, vol. 10, no. 6, pp. 3739–3758, 2010.
- [99] M. Meyyappan, L. Delzeit, A. Cassell, and D. Hash, “Carbon nanotube growth by PECVD: a review,” *Plasma Sources Sci. Technol.*, vol. 12, no. 2, pp. 205–216, May 2003.
- [100] Z. Chen *et al.*, “Large current carbon nanotube emitter growth using nickel as a buffer layer,” *Nanotechnology*, vol. 18, no. 9, p. 95604, 2007.
- [101] a. M. Rao, D. Jacques, R. C. Haddon, W. Zhu, C. Bower, and S. Jin, “In situ-grown carbon nanotube array with excellent field emission characteristics,” *Appl. Phys. Lett.*, vol. 76, no. 25, p. 3813, 2000.
- [102] a. L. Prudnikava, B. G. Shulitski, V. a. Labunov, a. Navitski, V. Sakharuk, and G. Müller, “Efficient high-current field emission from arrays of CNT columns,” *Tech. Dig. - 2009 22nd Int. Vac. Nanoelectron. Conf. IVNC 2009*, pp. 257–258, 2009.
- [103] Z. Chen *et al.*, “Ultrahigh-current field emission from sandwich-grown well-aligned uniform multi-walled carbon nanotube arrays with high adherence strength.,” *Nanotechnology*, vol. 18, no. 26, p. 265702, 2007.
- [104] S. Kato and T. Noguchi, “High Current Density Field Emission Electron Source,” in *Carbon Nanotube and Related Field Emitters: Fundamentals and Applications*, Weinheim: WILEY-VCH, 2010, pp. 373–388.
- [105] H. Liu, T. Noguchi, and S. Kato, “Influence of RuO₂ nanoparticles on electron

References

- emission from carbon nanotubes,” *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, vol. 25, no. 6, p. 1814, 2007.
- [106] K.-Y. Dong, Y. D. Lee, B. H. Kang, J. Choi, and B.-K. Ju, “Design of a multi-walled carbon nanotube field emitter with micro vacuum gauge,” *Nanoscale Res. Lett.*, vol. 8, no. 1, p. 143, 2013.
- [107] W. Lei, Z. Zhu, C. Liu, X. Zhang, B. Wang, and A. Nathan, “High-current field-emission of carbon nanotubes and its application as a fast-imaging X-ray source,” *Carbon N. Y.*, vol. 94, pp. 687–693, 2015.
- [108] J. Chen, B. Yang, X. Liu, J. Yang, L. Cui, and X. Yan, “Large field emission current and density from robust carbon nanotube cathodes for continuous and pulsed electron sources,” *Sci. China Mater.*, vol. 60, no. 4, pp. 335–342, 2017.
- [109] K. R. Izrael’yants, a. L. Musatov, a. B. Ormont, E. G. Chirkova, and E. F. Kukovitsky, “Emission characteristics of planar field electron emitters containing carbon nanotubes operating in the high current density mode,” *Carbon N. Y.*, vol. 48, no. 7, pp. 1889–1896, Jun. 2010.
- [110] C. Zhao, S. Aditya, S. Wang, J. Miao, and X. Xia, “A Wideband Microfabricated Ka-Band Planar Helix Slow-Wave Structure,” *IEEE Trans. Electron Devices*, vol. 63, no. 7, pp. 2900–2906, 2016.
- [111] M. S. Mohamed Saheed, N. M. Mohamed, and Z. A. Burhanudin, “Effect of different catalyst deposition technique on aligned multiwalled carbon nanotubes grown by thermal chemical vapor deposition,” *J. Nanomater.*, vol. 2014, 2014.
- [112] S. Wang, S. Aditya, and C. Zhao, “Spatial power combining of Ka-band microfabricated TWTs based on a planar helix slow-wave structure,” *2016 IEEE Int.*

References

- Vac. Electron. Conf. IVEC 2016*, pp. 29–30, 2016.
- [113] F. Malek, “THE ANALYTICAL DESIGN OF A FOLDED WAVEGUIDE TRAVELING WAVE TUBE AND SMALL SIGNAL GAIN ANALYSIS USING MADEY’S THEOREM,” *Progress In Electromagnetics Research*, vol. 98. pp. 137–162, 2009.
- [114] A. S. Gilmour, “Electron Beams,” in *Principles of Traveling-Wave Tubes*, Boston: Artech House, 1994, p. 155.
- [115] S. Esconjauregui *et al.*, “Measurement of area density of vertically aligned carbon nanotube forests by the weight-gain method,” *J. Appl. Phys.*, vol. 113, no. 14, 2013.
- [116] D. N. Futaba *et al.*, “Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes,” *Nat. Mater.*, vol. 5, no. 12, pp. 987–994, 2006.
- [117] D. Jiang, T. Wang, S. Chen, L. Ye, and J. Liu, “Paper-mediated controlled densification and low temperature transfer of carbon nanotube forests for electronic interconnect application,” *Microelectron. Eng.*, vol. 103, pp. 177–180, 2013.
- [118] M. Baro, D. Gogoi, A. R. Pal, N. C. Adhikary, H. Bailung, and J. Chutia, “Pulsed PECVD for Low-temperature Growth of Vertically Aligned Carbon Nanotubes,” *Chem. Vap. Depos.*, vol. 20, no. 4-5–6, pp. 161–169, Jun. 2014.
- [119] M. . Fransen, T. . van Rooy, and P. Kruit, “Field emission energy distributions from individual multiwalled carbon nanotubes,” *Appl. Surf. Sci.*, vol. 146, no. 1–4, pp. 312–327, 1999.
- [120] M. Wang, Z. H. Li, X. F. Shang, X. Q. Wang, and Y. B. Xu, “Field-enhancement factor for carbon nanotube array,” *J. Appl. Phys.*, vol. 98, no. 1, pp. 1–5, 2005.

References

- [121] G. Chen, S. Neupane, W. Li, L. Chen, and J. Zhang, “An increase in the field emission from vertically aligned multiwalled carbon nanotubes caused by NH₃ plasma treatment,” *Carbon N. Y.*, vol. 52, no. Dc, pp. 468–475, 2013.
- [122] C. J. Edgcombe and U. Valdrè, “Experimental and computational study of field emission characteristics from amorphous carbon single nanotips grown by carbon contamination. I. Experiments and computation,” *Philos. Mag. Part B*, vol. 82, no. 9, pp. 987–1007, 2002.
- [123] W. Wang and Z. Li, “Comment on slope of nonlinear FN plot and field enhancement factor,” no. 1, pp. 1–6.
- [124] K.-Y. Wang, C.-Y. Liao, and H.-C. Cheng, “Field-Emission Characteristics of the Densified Carbon Nanotube Pillars Array,” *ECS J. Solid State Sci. Technol.*, vol. 5, no. 9, pp. M99–M103, 2016.
- [125] K. Zhang *et al.*, “Facile synthesis of high density carbon nanotube array by a deposition-growth-densification process,” *Carbon N. Y.*, vol. 114, pp. 435–440, 2017.
- [126] N. Sinha and J. T. W. Yeow, “Modeling of the Behavior of Random Carbon Nanotubes During Field Emission,” in *MEMS, NANO and Smart Systems, 2005. Proceedings. 2005 International Conference*, 2005.
- [127] Y. D. Lim *et al.*, “Temperature-dependent selective growth of carbon nanotubes in Si / SiO₂ structures for field emitter array applications,” *Mater. Res. Bull.*, vol. 95, pp. 129–137, 2017.
- [128] A. Ramirez, N. Latorre, R. Mallada, R. M. Tiggelaar, and A. Monzón, “Unraveling the growth of vertically aligned multi-walled carbon nanotubes by chemical vapor deposition,” *Mater. Res. Express*, vol. 1, no. 4, p. 45604, 2013.

References

- [129] K. B. K. Teo *et al.*, “Plasma enhanced chemical vapour deposition carbon nanotubes/nanofibres how uniform do they grow?,” *Nanotechnology*, vol. 14, no. 2, pp. 204–211, Feb. 2003.
- [130] C. Bower, W. Zhu, S. Jin, and O. Zhou, “Plasma-induced alignment of carbon nanotubes,” *Appl. Phys. Lett.*, vol. 77, no. 6, p. 830, 2000.
- [131] Z. P. Huang, D. Z. Wang, J. G. Wen, M. Sennett, H. Gibson, and Z. F. Ren, “Effect of nickel, iron and cobalt on growth of aligned carbon nanotubes,” *Appl. Phys. A Mater. Sci. Process.*, vol. 74, no. 3, pp. 387–391, 2002.
- [132] W. W. Liu, C. X. Lu, X. L. Wang, K. Liang, and B. K. Tay, “In situ fabrication of three-dimensional, ultrathin graphitae/carbon nanotube/NiO composite as binder-free electrode for high-performance energy storage,” *J. Mater. Chem. A*, vol. 3, no. 2, pp. 624–633, 2015.
- [133] J. K. Radhakrishnan *et al.*, “Growth of multiwalled carbon nanotube arrays by chemical vapour deposition over iron catalyst and the effect of growth parameters,” *Appl. Surf. Sci.*, vol. 255, no. 12, pp. 6325–6334, Apr. 2009.
- [134] F. F. Dall’agnol and D. den Engelsen, “Field emission from non-uniform carbon nanotube arrays,” *Nanoscale Res. Lett.*, vol. 8, no. 1, p. 319, 2013.
- [135] K. Y. Wang, C. H. Chou, C. Y. Liao, Y. R. Li, and H. C. Cheng, “Densification effects of the carbon nanotube pillar array on field-emission properties,” *Jpn. J. Appl. Phys.*, vol. 55, no. 6, 2016.
- [136] N. Liu, G. Fang, W. Zeng, H. Zhou, H. Long, and X. Zhao, “Enhanced field emission from three-dimensional patterned carbon nanotube,” *J. Mater. Chem.*, vol. 22, pp. 3478–3484, 2012.

References

- [137] C. J. Shearer, A. Fahy, M. G. Barr, K. E. Moore, P. C. Dastoor, and J. G. Shapter, “Field emission from single-, double-, and multi-walled carbon nanotubes chemically attached to silicon,” *J. Appl. Phys.*, vol. 111, no. 4, 2012.
- [138] S. Parveen, A. Kumar, S. Husain, and M. Husain, “Fowler Nordheim theory of carbon nanotube based field emitters,” *Phys. B Condens. Matter*, vol. 505, no. September 2016, pp. 1–8, 2017.
- [139] E. Minoux, O. Groening, and K. Teo, “Achieving high-current carbon nanotube emitters,” *Nano Lett.*, vol. 15, no. 11, pp. 2135–2138, 2005.
- [140] Y. D. Lim, Q. Kong, S. Wang, C. W. Tan, B. K. Tay, and S. Aditya, “Enhanced field emission properties of carbon nanotube films using densification technique,” *Appl. Surf. Sci.*, 2017.
- [141] W. S. Su, T. C. Leung, and C. T. Chan, “Work function of single-walled and multiwalled carbon nanotubes: First-principles study,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 76, no. 23, pp. 2–9, 2007.
- [142] H. Liu, S. Kato, and Y. Saito, “Effect of Cathode–Anode Distance on Field Emission Properties for Carbon Nanotube Film Emitters,” *Jpn. J. Appl. Phys.*, vol. 48, no. 1, p. 15007, Jan. 2009.
- [143] D. Varshney, A. V. Sumant, B. R. Weiner, and G. Morell, “Growth of carbon nanotubes on spontaneously detached free standing diamond films and their field emission properties,” *Diam. Relat. Mater.*, vol. 30, pp. 42–47, 2012.
- [144] G. Zhong, R. Xie, J. Yang, and J. Robertson, “Single-step CVD growth of high-density carbon nanotube forests on metallic Ti coatings through catalyst engineering,” *Carbon N. Y.*, vol. 67, no. 1, pp. 680–687, 2014.

References

- [145] Z. Li *et al.*, “High current field emission from individual non-linear resistor ballasted carbon nanotube cluster array,” *Carbon N. Y.*, vol. 89, pp. 1–7, 2015.
- [146] J. Y. Huang, K. Kempa, S. H. Jo, S. Chen, and Z. F. Ren, “Giant field enhancement at carbon nanotube tips induced by multistage effect,” *Appl. Phys. Lett.*, vol. 87, no. 5, pp. 167–169, 2005.
- [147] J. H. Choi *et al.*, “Enhanced electron emission from carbon nanotubes through density control using in situ plasma treatment of catalyst metal,” *J. Appl. Phys.*, vol. 94, no. 1, p. 487, 2003.
- [148] X. Yang *et al.*, “Synthesis and field emission properties of carbon nanotubes grown in ethanol flame based on a photoresist-assisted catalyst annealing process,” *Appl. Surf. Sci.*, vol. 255, no. 18, pp. 7905–7911, 2009.
- [149] J. Bonard, M. Croci, C. Klinke, R. Kurt, and O. Noury, “Carbon nanotube films as electron field emitters,” *Carbon N. Y.*, vol. 40, pp. 1715–1728, 2002.
- [150] S. Neupane, M. Lastres, M. Chiarella, W. Li, Q. Su, and G. Du, “Synthesis and field emission properties of vertically aligned carbon nanotube arrays on copper,” *Carbon N. Y.*, vol. 50, no. 7, pp. 2641–2650, 2012.
- [151] S. C. et al. Ray, “High-Temperature Annealing Effects on Multiwalled Carbon Nanotubes: Electronic Structure, Field Emission and Magnetic Behaviors,” *J. Nanosci. Nanotechnol.*, vol. 9, no. 12, pp. 6799–6805, 2009.
- [152] D. Tan *et al.*, “Improved RF Isolation Using Carbon Nanotube Fence-Wall for 3-D Integrated Circuits and Packaging,” *IEEE Microw. Wirel. Components Lett.*, vol. 25, no. 6, pp. 355–357, 2015.
- [153] N. Liu *et al.*, “Synthesis of patterned carbon nanotube arrays for field emission using a

References

- two layer Sn/Ni catalyst in an ethanol flame,” *Diam. Relat. Mater.*, vol. 18, no. 11, pp. 1375–1380, Nov. 2009.
- [154] M. Khaneja *et al.*, “High Field Emission Current Density from Patterned Carbon Nanotube Field Emitter Arrays with Random Growth,” *J. Nanosci. Nanotechnol.*, vol. 15, no. 5, pp. 3846–3851, 2015.
- [155] G. Bocharov and A. Eletskii, “Theory of Carbon Nanotube (CNT)-Based Electron Field Emitters,” *Nanomaterials*, vol. 3, no. 3, pp. 393–442, 2013.
- [156] L. Bokobza and J. Zhang, “Raman spectroscopic characterization of multiwall carbon nanotubes and of composites,” *Express Polym. Lett.*, vol. 6, no. 7, pp. 601–608, 2012.
- [157] a. Ferrari and J. Robertson, “Interpretation of Raman spectra of disordered and amorphous carbon,” *Phys. Rev. B*, vol. 61, no. 20, pp. 14095–14107, May 2000.
- [158] A. Mathur, M. Tweedie, S. S. Roy, P. D. Maguire, and J. a McLaughlin, “Electrical and Raman spectroscopic studies of vertically aligned multi-walled carbon nanotubes,” *J. Nanosci. Nanotechnol.*, vol. 9, no. 7, pp. 4392–4396, 2009.
- [159] Y. Shen, Y. Qiao, Z. He, and S. Yu, “Enhancing electrical conductivity and electron field emission property of free standing diamond films by employing embedded Ag nanoparticles,” *Mater. Lett.*, vol. 139, pp. 322–324, 2015.
- [160] L. Zhu, J. Xu, Y. Xiu, Y. Sun, D. W. Hess, and C. P. Wong, “Growth and electrical characterization of high-aspect-ratio carbon nanotube arrays,” *Carbon N. Y.*, vol. 44, no. 2, pp. 253–258, 2006.
- [161] K. J. Kim, W.-R. Yu, J. H. Youk, and J. Lee, “Factors governing the growth mode of carbon nanotubes on carbon-based substrates,” *Phys. Chem. Chem. Phys.*, vol. 14, no. 40, pp. 14041–8, Oct. 2012.

References

- [162] Y. J. Jung, B. Wei, R. Vajtai, and P. M. Ajayan, "Mechanism of Selective Growth of Carbon Nanotubes on SiO₂ / Si Patterns," *Nano Lett.*, vol. 3, no. 4, pp. 2–5, 2003.
- [163] M. Pinault, M. Mayne-L'Hermite, C. Reynaud, O. Beyssac, J. N. Rouzaud, and C. Clinard, "Carbon nanotubes produced by aerosol pyrolysis: Growth mechanisms and post-annealing effects," *Diam. Relat. Mater.*, vol. 13, no. 4–8, pp. 1266–1269, 2004.
- [164] A. V. Goncharenko, M. M. Dvoynenko, H. C. Chang, and J. K. Wang, "Electric field enhancement by a nanometer-scaled conical metal tip in the context of scattering-type near-field optical microscopy," *Appl. Phys. Lett.*, vol. 88, no. 10, pp. 1–4, 2006.
- [165] A. V. Goncharenko, H. C. Chang, and J. K. Wang, "Electric near-field enhancing properties of a finite-size metal conical nano-tip," *Ultramicroscopy*, vol. 107, no. 2–3, pp. 151–157, 2007.
- [166] C. L. Cheung, A. Kurtz, H. Park, and C. M. Lieber, "Diameter-controlled synthesis of carbon nanotubes," *J. Phys. Chem. B*, vol. 106, no. 10, pp. 2429–2433, 2002.
- [167] M. Chhowalla, C. Ducati, N. L. Rupesinghe, K. B. K. Teo, and G. a J. Amaratunga, "Field emission from short and stubby vertically aligned carbon nanotubes," *Appl. Phys. Lett.*, vol. 79, no. 13, pp. 2079–2081, 2001.
- [168] T. T. Ebbesen, T. W., Lezec H. J., Hiura H., Bennett J. W., Ghaemi H. F., "Electrical conductivity of individual carbon nanotubes," *Nature*, vol. 382. pp. 54–56, 1996.
- [169] K. S. Hazra, T. Gigras, and D. S. Misra, "Tailoring the electrostatic screening effect during field emission from hollow multiwalled carbon nanotube pillars," *Appl. Phys. Lett.*, vol. 98, no. 12, p. 123116, 2011.
- [170] H. Sato, K. Haruki, M. Watanabe, K. Hata, and Y. Saito, "Effect of geometry of a vertically aligned carbon nanotube pillar array on its field-emission properties," *Surf.*

References

- Interface Anal.*, vol. 44, no. 6, pp. 776–779, 2012.
- [171] Z. Zhang, Y. A. Zhou, and Y. Yue, “Growth carbon nanotubes directly on pristine silicon substrates,” *Int. J. Nanosci.*, vol. 5, no. 4 & 5, pp. 433–439, 2006.
- [172] W. K. Choi, C. K. Choo, and Y. F. Lu, “Electrical characterization of rapid thermal annealed radio frequency sputtered silicon oxide films,” *J. Appl. Phys.*, vol. 80, no. 10, p. 5837, 1996.
- [173] V. A. Labunov, B. G. Shulitski, A. L. Prudnikava, Y. P. Shaman, and A. S. Basaev, “The effect of gas-dynamic factors on selective carbon-nanotube synthesis by injection CVD method for field-emission cathodes,” *J. Soc. Inf. Disp.*, vol. 17, no. 5, pp. 489–495, 2009.
- [174] J. Sengupta, A. Jana, N. D. Pradeep Singh, and C. Jacob, “Effect of growth temperature on the CVD grown Fe filled multi-walled carbon nanotubes using a modified photoresist,” *Mater. Res. Bull.*, vol. 45, no. 9, pp. 1189–1193, 2010.
- [175] X. Bai, D. Li, Y. Wang, and J. Liang, “Effects of temperature and catalyst concentration on the growth of aligned carbon nanotubes,” *Tsinghua Sci. Technol.*, vol. 10, no. 6, pp. 729–735, 2005.
- [176] Y. D. Lim, A. Avramchuck, D. Grapov, B. K. Tay, A. Sheel, and V. Labunov, “Field emission characteristics of short CNT bundles,” in *International Vacuum Electronics Conference*, 2016.
- [177] D. L. Niemann *et al.*, “Carbon Nanotube Field Emission Devices with Integrated Gate for High Current Applications,” *2008 8th IEEE Conf. Nanotechnol.*, pp. 456–459, 2008.
- [178] N. Dahal and V. Chikan, “Phase-controlled synthesis of iron silicide (Fe₃Si and FeSi

References

- 2) nanoparticles in solution,” *Chem. Mater.*, vol. 22, no. 9, pp. 2892–2897, 2010.
- [179] N. Ohtsu, M. Oku, K. Satoh, and K. Wagatsuma, “Dependence of core-level XPS spectra on iron silicide phase,” *Appl. Surf. Sci.*, vol. 264, pp. 219–224, 2013.
- [180] R. Kar *et al.*, “Effect of substrate heating and microwave attenuation on the catalyst free growth and field emission of carbon nanotubes,” *Carbon N. Y.*, vol. 94, pp. 256–265, 2015.
- [181] S. Handuja, P. Srivastava, and V. D. Vankar, “On the growth and microstructure of carbon nanotubes grown by thermal chemical vapor deposition,” *Nanoscale Res. Lett.*, vol. 5, no. 7, pp. 1211–1216, 2010.
- [182] J. D. McBrayer, “Diffusion of Metals in Silicon Dioxide,” *J. Electrochem. Soc.*, vol. 133, no. 6, p. 1242, 1986.
- [183] A. A. Istratov, H. Hieslmair, and E. R. Weber, “Iron and its complexes in silicon,” *Appl. Phys. A Mater. Sci. Process.*, vol. 69, no. 1, pp. 13–44, 1999.
- [184] M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, and R. Saito, “Perspectives on carbon nanotubes and graphene Raman spectroscopy,” *Nano Lett.*, vol. 10, no. 3, pp. 751–758, 2010.
- [185] M. a Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, a Jorio, and R. Saito, “Studying disorder in graphite-based systems by Raman spectroscopy,” *Phys. Chem. Chem. Phys.*, vol. 9, no. 11, pp. 1276–1291, 2007.
- [186] C. J. Lee, J. Park, Y. Huh, and J. Yong Lee, “Temperature effect on the growth of carbon nanotubes using thermal chemical vapor deposition,” *Chem. Phys. Lett.*, vol. 343, no. 1–2, pp. 33–38, 2001.
- [187] F. A. Rabbani, Z. O. Malaibari, M. A. Atieh, and A. Jamie, “Catalytic synthesis of

References

- substrate-free, aligned and tailored high aspect ratio multiwall carbon nanotubes in an ultrasonic atomization head CVD reactor,” *J. Nanomater.*, vol. 2016, no. 4189456, pp. 1–10, 2016.
- [188] S. V. Kovesnikov and G. A. Rozgonyi, “Iron diffusivity in silicon: Impact of charge state,” *Appl. Phys. Lett.*, vol. 860, no. 1995, p. 860, 1995.
- [189] P. Yang, L. Liu, J. Mo, and W. Yang, “Characterization of PECVD grown porous SiO₂ Thin Films With Potential Application in an Uncooled Infrared Detector,” *Semicond. Sci. Technol.*, vol. 25, no. 4, p. 45017, 2010.
- [190] H. Liang, L. Delian, C. Xian, Y. Li, and Z. Yuqing, “The deposition of a thick tetrahedral amorphous carbon film by argon ion bombardment,” *Appl. Surf. Sci.*, vol. 258, no. 10, pp. 4794–4800, Mar. 2012.
- [191] A. Cao, P. M. Ajayan, G. Ramanath, R. Baskaran, and K. Turner, “Silicon oxide thickness-dependent growth of carbon nanotubes,” *Appl. Phys. Lett.*, vol. 84, no. 1, pp. 109–111, 2004.
- [192] M. Aksak, S. Kir, and Y. Selamet, “Effect of the growth temperature on carbon nanotubes grown by thermal chemical vapor deposition method,” *Iyte.Edu.Tr*, vol. 1, no. 3, pp. 281–284, 2009.
- [193] C. P. Juan and J. H. Lin, “Ultra-low turn-on field and ultra-high field emission current density from pillar array design of carbon nanotubes with optimum R/H ratio,” *Proc. - Winter Simul. Conf.*, pp. 231–233, 2013.
- [194] S.-D. Liang and L. Chen, “Generalized Fowler-Nordheim theory of field emission of carbon nanotubes,” *Phys. Rev. Lett.*, vol. 101, no. 2, p. 27602, 2008.
- [195] J.-M. Bonard, C. Klinke, K. a. Dean, and B. Coll, “Degradation and failure of carbon

References

- nanotube field emitters,” *Phys. Rev. B*, vol. 67, no. 11, p. 115406, 2003.
- [196] J. Peng *et al.*, “The roles of apex dipoles and field penetration in the physics of charged, field emitting, single-walled carbon nanotubes,” *J. Appl. Phys.*, vol. 104, no. 1, 2008.
- [197] Y. D. LIM *et al.*, “Field Emission Properties of SiO₂-wrapped CNT Field Emitter,” *Nanotechnology*, vol. 29, p. 15202, 2017.
- [198] C. Jin, J. Wang, M. Wang, J. Su, and L. M. Peng, “In-situ studies of electron field emission of single carbon nanotubes inside the TEM,” *Carbon N. Y.*, vol. 43, no. 5, pp. 1026–1031, 2005.
- [199] V. J. Scott, H. Manohara, R. Toda, and L. Del Castillo, “Robust CNT field emitters : patterning , growth , transfer , and in situ anchoring,” *Nanotechnology*, vol. 27, no. 49, p. 494022, 2016.
- [200] Y. Sun, J. T. W. Yeow, and D. A. Jaffray, “Design and fabrication of carbon nanotube field-emission cathode with coaxial gate and ballast resistor,” *Small*, vol. 9, no. 20, pp. 3385–3389, 2013.
- [201] P. Helfenstein, V. a. Guzenko, H. W. Fink, and S. Tsujino, “Electron beam collimation with a 40,000 tip double-gate metal field emitter array and in-situ control of nanotip sharpness distribution,” *2013 26th Int. Vac. Nanoelectron. Conf. IVNC 2013*, vol. 43306, pp. 1–7, 2013.
- [202] L. Singh, M. Walker, and G. Sanborn, “Operation of Spindt-Type, Carbon Nanotube Cold Cathodes in a Hall Effect Thruster Environment,” in *Iepc*, 2013, pp. 1–13.
- [203] W. Zhu, C. Bower, O. Zhou, G. Kochanski, and S. Jin, “Large current density from carbon nanotube field emitters,” *Appl. Phys. Lett.*, vol. 75, no. 6, pp. 873–875, 1999.

References

- [204] Y. Zuo, Y. Ren, Z. Wang, X. Han, and L. Xi, “Enhanced field emission and hysteresis characteristics of aligned carbon nanotubes with Ti decoration,” *Org. Electron. physics, Mater. Appl.*, vol. 14, no. 9, pp. 2306–2314, 2013.
- [205] Z. Lin, S. Young, C. Hsiao, S. Chang, and C. Huang, “Improved field emission properties of Ag-decorated multi-walled carbon nanotubes,” *Ieee Photonics Technol. Lett.*, vol. 25, no. 11, pp. 1017–1019, 2013.
- [206] Q. Zhang, D. J. Yang, S. G. Wang, S. F. Yoon, and J. Ahn, “Influences of temperature on the Raman spectra of single-walled carbon nanotubes,” *Smart Mater. Struct.*, vol. 15, no. 1, pp. S1–S4, 2006.
- [207] T. W. Weng, Y. H. Lai, and K. Y. Lee, “Area effect of patterned carbon nanotube bundle on field electron emission characteristics,” *Appl. Surf. Sci.*, vol. 254, no. 23, pp. 7755–7758, 2008.
- [208] A. Rokhlenko and J. L. Lebowitz, “Space charge limited two-dimensional electron flow in a rectangular geometry,” *J. Appl. Phys.*, vol. 102, no. 2, 2007.
- [209] H. Ihara *et al.*, “Electric field concentration at electrode edge with decreasing amorphous silicon defect density,” *J. Non. Cryst. Solids*, vol. 198–200, no. PART 1, pp. 326–329, 1996.
- [210] J. T. O’Brien, J. S. Prell, A. I. S. Holm, and E. R. Williams, “Effects of Electron Kinetic Energy and Ion-Electron Inelastic Collisions in Electron Capture Dissociation Measured Using Ion Nanocalorimetry,” *J. Am. Soc. Mass Spectrom.*, vol. 19, no. 6, pp. 772–779, 2008.
- [211] N. H. Langton, “The Electric or Magnetic Fields External to a Series of Corners,” *J. Electrostat.*, vol. 2, pp. 351–366, 1977.

References

- [212] E. G. Pogorelov, A. I. Zhbanov, and Y. C. Chang, “Field enhancement factor and field emission from a hemi-ellipsoidal metallic needle,” *Ultramicroscopy*, vol. 109, no. 4, pp. 373–378, 2009.
- [213] C. S. Kumarasinghe, M. Premaratne, Q. Bao, and G. P. Agrawal, “Theoretical analysis of hot electron dynamics in nanorods,” *Sci. Rep.*, vol. 5, no. 1, p. 12140, 2015.
- [214] S. Y. Lee *et al.*, “The roles of ruthenium nanoparticles decorated on thin multi-walled carbon nanotubes in the enhancement of field emission properties,” *Appl. Phys. Lett.*, vol. 100, no. 2, pp. 1–4, 2012.