

**GROWTH OF CARBON NANOSTRUCTURE
ARRAYS ON NICKEL ELECTROPLATED
COPPER SUBSTRATE**

ROSZAINI BINTI MD SALLEH

UNIVERSITI SAINS MALAYSIA

2016

**GROWTH OF CARBON NANOSTRUCTURE ARRAYS
ON NICKEL ELECTROPLATED COPPER SUBSTRATE**

by

ROSZAINI BINTI MD SALLEH

Thesis submitted in fulfilment of the requirements

for the degree of

Master in Science

September 2016

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful.

Alhamdulillah, all praises to Allah for His blessing and willness in completing this thesis. My greatest appreciation is forwarded to my main Supervisor Prof Dr Abdul Rahman Bin Mohamed and my co-supervisor Dr Yeoh Wei Ming for their continuous support, being such a great mentors and taking their busy time to supervise and giving valuable comments and guidance throughout my study.

I would also like to thank Prof. Dr. Azlina Harun @ Kamaruddin, Dean of the School of Chemical Engineering USM and all lecturers, for their continuous motivation, and invaluable help in postgraduate affairs throughout my studies. I would also like to extend my sincere appreciation to laboratory technicians and administrative staff of the School of Chemical Engineering USM for the assistance along journey of my study.

Then, I would like to thank my beloved family, especially my father, Md Salleh Bin Yop, all family members and also my husband, Fakrularif bin Abd Latif for their encouragement, support and prayers throughout my pursuance of master degree in Universiti Sains Malaysia. Words failed to express my appreciation for their support and persistent confidence in me.

Special thanks to all Project team members from Alterra Corporation (M) Sdn Bhd, Project Leader, Mr KB Lim, from Polytool, MST Technology, Penchem

Technologies and not forget warmest thanks to all my friends in USM especially CNTs and graphene group who continuously give me guidances and moral supports for me to finish my master study.

Last but not least I am very much indebted to CREST (Project No: 6050285) who providing me financial support throughout my research study.

Thank you very much!

ROSZAINI

SEPTEMBER 2016

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iv
LIST OF TABLES	ix
LIST OF FIGURES	xiii
LIST OF PLATES	xviii
LIST OF ABBREVIATIONS	xix
LIST OF SYMBOLS	xx
ABSTRAK	xxi
ABSTRACT	xxiii
CHAPTER ONE : INTRODUCTION	
1.1 Electronic Industry	1
1.2 Electronic Package	2
1.2.1 Heat Spreader	3
1.2.2 Thermal Interface Materials	4
1.3 Nanotechnology and Nanomaterials	5
1.4 Electroplating	6
1.5 CNS Growth Mechanism	7
1.6 Problem Statements	9
1.7 Objectives	11
1.8 Scope of Study	12
1.9 Organization of the Thesis	13

CHAPTER TWO : LITERATURE REVIEW

2.1	Carbon Nanostructures (CNS)	16
2.2	Thin Film Coating	20
	2.2.1 Physical Vapour Deposition	20
	2.2.2 Solution-Based Catalyst Precursor and Coating Methods	21
2.3	Electroplating	23
	2.3.1 Mechanism of Nickel Electroplating	23
	2.3.2 Electrolyte Bath	25
	2.3.3 Nickel Plating Parameters	27
2.4	Synthesis of CNS	31
	2.4.1 Electric Arc-Discharge (EAD)	32
	2.4.2 Laser Ablation	33
	2.4.3 Chemical Vapour Deposition(CVD)	34
2.5	Synthesis of CNS via Catalytic Chemical Vapour Deposition (CCVD)	36
	2.5.1 Carbon Precursor	36
	2.5.2 Catalyst	38
	2.5.2 (a) Active Catalyst Size	43
	2.5.3 Substrate	44
	2.5.4 Process Study of CCVD	46

CHAPTER THREE : MATERIALS AND METHODS

3.1	Materials and Chemicals	52
3.2	Overall Experimental Work	53
	3.2.1 Brief Description of Experimental Work	53

3.2.2	Experimental Procedures	55
3.2.2 (a)	Electrolyte Preparation Method	55
3.2.2 (b)	Catalyst Deposition Method using Electroplating	56
3.2.2 (c)	Production of CNS via CCVD	56
3.3	Experimental Set-Up	57
3.3.1	Electroplating Unit	57
3.3.2	CNS Growth Rig	58
3.4	The Synthesis Parameter Variations	62
3.4.1	Process Study for Electroplating to Form Nickel Plated Catalyst	62
3.4.2	Process Study for The Synthesis of CNS <i>via</i> CCVD	63
3.5	Characterizations	63
3.5.1	Scanning Electron Microscopy (SEM)	63
3.5.2	Energy Dispersive X-ray spectroscopy (EDX)	64
3.5.3	X-Ray Fluorescences (XRF)	64
3.5.4	Atomic Force Microscopy (AFM)	64
3.5.5	Raman Spectroscopy	65
3.5.6	Transmission Electron Microscopy (TEM)	66
3.5.7	Thermogravimetric Analysis (TGA)	66
 CHAPTER FOUR : RESULTS AND DISCUSSION		
4.1	Preliminary Study	68
4.1.1	The Effect of Heat on Nickel Plated Copper Heat Spreader	68
4.2	Process Study of Electroplating Process	70

4.2.1	Effect of Current Density on the Nickel Plated Catalyst on the Copper Substrate	71
4.2.1 (a)	SEM and EDX Characterization	72
4.2.1 (b)	XRF Characterization	75
4.2.1 (c)	AFM Characterization	78
4.2.2	Effect of Plating Time to the Nickel Plated on the Copper Substrate	81
4.2.2 (a)	SEM and EDX Characterization	82
4.2.2 (b)	XRF Characterization	85
4.2.2 (c)	AFM Characterization	87
4.3	Performance of Electroplating Parameters Towards CNS Growth	89
4.3.1	Effect of Current Density to the CNS Growth	89
4.3.1 (a)	SEM and EDX Characterization for CNS Growth	89
4.3.1 (b)	TEM Characterization	91
4.3.1 (c)	TGA Characterization	94
4.3.1 (d)	Raman Spectroscopy Characterization	97
4.3.2	Effect of Plating Time to the CNS Growth	99
4.3.2 (a)	SEM and EDX Characterization for CNS Growth	99
4.3.2 (b)	TEM Characterization	101
4.3.2 (c)	TGA Characterization	103
4.3.2 (d)	Raman Spectroscopy Characterization	106
4.4	Process Study of CNS Growth	108
4.4.1	Effect of Reaction Temperature	109

4.4.1 (a)	SEM and EDX Characterization	109
4.4.1 (b)	TEM Characterization	112
4.4.1 (c)	TGA Characterization	113
4.4.1 (d)	Raman Spectroscopy Characterization	116
4.4.2	Effect of Reaction Time	118
4.4.2 (a)	SEM and EDX Characterization	118
4.4.2 (b)	TEM Characterization	120
4.4.2 (c)	TGA Characterization	122
4.4.2 (d)	Raman Spectroscopy Characterization	125
4.4.3	Effect of Flowrate of Acetylene (C ₂ H ₂)	127
4.4.3 (a)	SEM and EDX Characterization	127
4.4.3 (b)	TEM Characterization	129
4.4.3 (c)	TGA Characterization	132
4.4.3 (d)	Raman Spectroscopy Characterization	135

CHAPTER FIVE : CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusions	137
5.2	Recommendations	139

REFERENCES	140
-------------------	-----

APPENDICES

LIST OF TABLES

		Page
Table 2.1	Properties of various types of CNS	19
Table 2.2	Reviews on the nickel plating parameters	28
Table 2.3	Comparison of CNTs synthesis methods (Rafique & Iqbal 2011)	36
Table 2.4	Reviews of catalysts and substrates for CNS growth used in previous study	39
Table 2.5	Review on the process study using CCVD	47
Table 3.1	List of chemicals and reagents	52
Table 3.2	Major components of the experiment CNS growth rig and their function	60
Table 3.3	Range of plating parameters	62
Table 3.4	Range of parameters for CCVD	63
Table 4.1	List of constant parameters	71
Table 4.2	Range of grains size at different current density	72
Table 4.3	Elemental composition of nickel plated on the copper substrate at different current density	75
Table 4.4	Thickness of nickel plated on copper substrate at different current densities	76

Table 4.5	Grain size and surface roughness of nickel plated catalyst at different current density	79
Table 4.6	List of constant parameters	81
Table 4.7	Range of grain size at different current density	82
Table 4.8	Elemental composition of nickel plated on the copper substrate at different plating time	84
Table 4.9	Thickness of the nickel plated at different plating time	85
Table 4.10	Grain size and surface roughness of nickel plated layer at different plating time	87
Table 4.11	Weight percent of carbon and other elements at different current density	91
Table 4.12	Range of outer diameter CNS produced for nickel plated electroplated at different current density	94
Table 4.13	Percentage of residue and purity for carbon deposit on nickel plated at different current density	95
Table 4.14	On-set temperature, inflection and end temperature of CNS growth on nickel plated catalyst at different current density.	96
Table 4.15	I_D , I_G and I_D/I_G ratio for carbon deposit on nickel plated at different current density	98

Table 4.16	Weight percent of carbon and other elements at different plating time	101
Table 4.17	Range diameter of CNS growth on nickel plated at different plating time	103
Table 4.18	Percentage of residue and purity for carbon deposit on nickel plated at different plating time	104
Table 4.19	On-set temperature, inflection and end temperature of CNS growth on nickel plated catalyst at different plating time	106
Table 4.20	I_D , I_G and I_D/I_G ratio for nickel plated at different plating time	108
Table 4.21	List of constant parameters	109
Table 4.22	Weight percent of carbon and other elements at different reaction temperature	111
Table 4.23	Range diameter of CNS growth on nickel plated at different reaction temperature	113
Table 4.24	Percentage of residue and purity for carbon deposit on nickel plated at different reaction temperature	114
Table 4.25	On-set temperature, inflection and end temperature of CNS growth on nickel plated catalyst at different reaction temperature.	115
Table 4.26	I_D , I_G and I_D/I_G ratio for CNS growth at different reaction temperature	117

Table 4.27	List of constant parameters	118
Table 4.28	Weight percent of carbon and other elements at different reaction time	120
Table 4.29	Range of outer diameter at different reaction time	122
Table 4.30	Percentage of residue and purity for carbon deposit on nickel plated at different reaction time	123
Table 4.31	On-set, inflection and end temperature for carbon deposit at different reaction time	125
Table 4.32	I_D , I_G and ratio I_D/I_G for all reaction time	126
Table 4.33	List of constant parameters	127
Table 4.34	Weight percent of carbon and other elements at different flowrate of acetylene	129
Table 4.35	Range of outer diameter CNS at different C_2H_2 flowrate	131
Table 4.36	Percentage of residue and purity for carbon deposit on nickel plated at different reaction time	133
Table 4.37	On-set, inflection and end temperature of carbon deposit at different flowrate of acetylene	134
Table 4.38	I_D, I_G and ratio of I_D/I_G for different acetylene flowrate	136

LIST OF FIGURES

		Page
Figure 1.1	Thermal properties of common heat spreader	3
Figure 1.2	TIM compressed between heat spreader and microprocessor chip	4
Figure 1.3	Tip growth model (Kumar & Ando 2010)	8
Figure 1.4	Base-growth model (Kumar & Ando 2010)	9
Figure 2.1	Several circumferential vector (Jacoboni, 2010)	17
Figure 2.2	Armchair (5,5), zigzag (8,0) and chiral (2,7) CNTs (Jacoboni, 2010)	17
Figure 2.3	Rolled of graphene sheets to form SWCNTs (Prasek et al. 2011)	18
Figure 2.4	Comparison of structures and diameter of CNTs, CNFs and CF (Kim et al. 2011)	18
Figure 2.5	Basic principle of nickel electroplating	24
Figure 2.6	Schematic diagram of arc- discharge method (Arora & Sharma 2014)	32
Figure 2.7	Schematic diagram of laser ablation (Szabó et al. 2010)	33

Figure 2.8	Schematic diagram of CVD in the simplest form (Kumar & Ando 2010)	35
Figure 2.9	CNTs tip and base growth from a substrate (Crossley et al. 2011)	45
Figure 3.1	Overall methodology flowchart	54
Figure 3.2	Schematic diagram of electroplating unit	57
Figure 3.3	Schematic diagram of the experimental rig set-up	59
Figure 3.4	Schematic diagram of horizontal quartz tube	62
Figure 4.1	Microhardness vs temperature ($^{\circ}\text{C}$) for nickel plated copper substrate (heat spreader)	70
Figure 4.2	SEM images of nickel plated on copper substrate for different current density at 30000 magnification (a)1 (b) 5 (c) 10 d) 20 and (e) 30 mA/cm ²	73
Figure 4.3	Percentage of non-uniformity vs current density	77
Figure 4.4	AFM images for the topography of nickel plating catalyst with plating current density (a) 1 (b) 5 (c) 10 (d) 20 and (e) 30 mA/cm ² (size for the images is 5 μm x 5 μm)	80
Figure 4.5	SEM images of nickel plated on copper substrate for different plating time at 30000 magnification (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 and (f) 60 min	83

Figure 4.6	Percentage of non-uniformity for nickel layer plated at different plating time of 10 to 60 mins	86
Figure 4.7	AFM images of the topography of nickel plated at 1mA/cm ² and different plating time (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 and (f) 60 min (size for the images is 5 μm x 5 μm)	88
Figure 4.8	SEM images for CNS growth at nickel plated catalyst electroplated at (a) 1 (b) 5 (c) 10 (d) 20 and (e) 30 mA/cm ²	90
Figure 4.9	TEM images for carbon deposit on the nickel plated catalyst electroplated at different current densities (a) 1 (b) 5 (c) 10 (d) 20 and (e) 30 mA/cm ²	93
Figure 4.10	CNS growth on 1 mA/cm ² nickel plated catalyst (a) low magnification (b) high magnification	94
Figure 4.11	TG-curve of CNS growth on the nickel plated catalyst plated at different current density	95
Figure 4.12	DTG curve of the carbon deposit by nickel plated catalyst electroplated at different current density	96
Figure 4.13	Raman spectrum of carbon deposit on nickel plated at different current density	98
Figure 4.14	SEM images of CNS growth on nickel plated catalyst plated at 1 mA/cm ² (a) 20 (b) 30 (c) 40 (d) 50 and (e) 60 min	100

Figure 4.15	TEM images of nickel plated catalyst plated at 1mA/cm ² (a) 20 (b) 30 (c) 40 (d) 50 and (e) 60 min	102
Figure 4.16	TG-curve for carbon deposit on nickel plated catalyst plated at different plating time	104
Figure 4.17	DTG curve of the carbon deposit by nickel plated catalyst plated at different plating time	106
Figure 4.18	Raman spectrum of carbon deposit on nickel plated electroplated at different plating time	107
Figure 4.19	SEM images of CNS growth at different reaction temperature (a) 400, (b) 500 (c) 600 (d) 700 and (e) 800 °C	110
Figure 4.20	TEM images of CNS growth at different reaction temperature (a) 500 (low magnification) (b) 500 (high magnification) (c) 600 and (d) 700 °C	112
Figure 4.21	TG-curve for carbon deposit at different reaction temperature	114
Figure 4.22	DTG curve of the carbon deposit at different reaction temperature	115
Figure 4.23	Raman spectrum of carbon deposit at different reaction temperature	117
Figure 4.24	SEM images of CNS growth at 600 °C different reaction time (a) 5 (b) 10 (c) 20 (d) 30 and (e) 40 min	119

Figure 4.25	TEM images of CNS growth at different reaction time (a) 5 (b) 10 (c) 20 (d) 30 and (e) 40 min	121
Figure 4.26	CNTs on reaction time at high magnification (a) 30 and (b) 40 min	122
Figure 4.27	TG-curve for carbon deposit at different reaction time	123
Figure 4.28	DTG curve of the carbon deposit at different reaction time	124
Figure 4.29	Raman spectrum of carbon deposit at different reaction time	126
Figure 4.30	SEM images of CNS growth at 600 °C at different acetylene flowrate (a) 10 (b) 15 (c) 20 (d) 25 and (e) 30 sccm	128
Figure 4.31	TEM images of CNS growth at different acetylene flowrate (a) 10 (b) 15 (c) 20 (d) 25 and (e) 30 sccm	130
Figure 4.32	TEM images at high magnification for formation of CNTs at different acetylene flowrate (a) 20 (b) 25 and (c) 30 sccm	131
Figure 4.33	TG-curve for carbon deposit at different acetylene flowrate	132
Figure 4.34	DTG curve of carbon deposit on nickel plated catalyst at different acetylene flowrate	134
Figure 4.35	Raman spectrum of carbon deposit at different flowrate of acetylene	135

LIST OF PLATES

		Page
Plate 4.1	Heat treatment for nickel plated on copper heat spreader	69
Plate 4.2	Nickel plated on copper heat spreader soften after heating	69

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
CCVD	Catalytic chemical vapour deposition
CNFs	Carbon nanofibers
CNS	Carbon nanostructures
CNTs	Carbon nanotubes
CVD	Chemical vapour deposition
DC	Direct current
DTG	Differential thermogravimetric
EDX	Energy Dispersive X-ray
G-CNTs	Graphitized carbon nanotubes
MWCNTs	Multiwalled carbon nanotubes
PVD	Physical vapour deposition
TIM	Thermal interface materials
SEM	Scanning electron microscopy
SWCNTs	Single walled carbon nanotubes
TEM	Transmission electron microscopy
TG	Thermogravimetric
TGA	Thermogravimetric analysis
XRF	X-ray fluorescence

LIST OF SYMBOLS

Al ₂ O ₃	Aluminium oxide
Ar	Argon
Co	Cobalt
°C	degree celcius
C ₂ H ₂	Acetylene
Cu	Copper
Fe	Iron
g/l	gram /litre
HV	kg _f /mm ²
H ₂ SO ₄	Sulphuric acic
H ₂	Hydrogen
mA/cm ²	miliampere/centimetre ²
min	minutes
Ni	Nickel
nm	Nanometre
N ₂	Nitrogen
Pd	Palladium
sccm	Standard cubic centimetre per minute
Si	Silicon
SiO ₂	Silicon oxide
wt %	Weight percent

PERTUMBUHAN TATASUSUNAN KARBON NANOSTRUKTUR DI ATAS SUBSTRAT KUPRUM TERELEKTROSADUR NIKEL

ABSTRAK

Sejak penemuan karbon nanotub (CNTs) pada tahun 1991 oleh Iijima, karbon nanostruktur (CNS) yang terdiri daripada karbon nanotub (CNTs) dan karbon nanofiber (CNFs), telah mendapat perhatian dalam kalangan pengkaji berikutan ciri-ciri luar biasa bahan ini. Banyak aktiviti penyelidikan dan penemuan baru berkaitan dengan potensi CNS telah diterokai dari semasa ke semasa. Salah satu potensi CNS ialah boleh digunakan sebagai bahan antara dua muka haba (TIM) dan diaplikasi di dalam bahan elektronik berikutan CNS merupakan pengalir haba yang baik. Jadi, kajian penyelidikan ini memberi tumpuan kepada sintesis CNS yang bekualiti dan berketumpatan tinggi di atas platform pada suhu pertumbuhan yang rendah ke arah merealisasikan potensi CNS sebagai TIM pada masa akan datang. Bahagian pertama dalam kajian penyelidikan ini ialah penyediaan bahan penyebaran haba menggunakan kaedah elektropenyaduran sebelum pertumbuhan CNS. Kaedah elektropenyaduran digunakan untuk menyalut pemangkin logam aktif, nikel ke atas kuprum yang bertindak sebagai substrat kerana mengandungi nilai pengalir haba yang tinggi manakala nikel dipilih sebagai pemangkin kerana berupaya menumbuhkan CNS dengan kepadatan yang tinggi dan ia juga merupakan bahan anti karat. Dua parameter dikaji dalam bahagian ini iaitu ketumpatan arus ($1-30 \text{ mA/cm}^2$) dan tempoh masa penyaduran (10 min-60 min). Semua sampel dicirikan menggunakan Mikroskop Electron Imbasan (SEM), Tenaga Serakan Sinar-X (EDX), Pendarkilau Sinar-X (XRF) dan Mikroskop Daya Atom (AFM). Untuk bahagian kedua, pertumbuhan CNS menggunakan Pemangkin Kimia Pemendapan Wap

(CCVD) di mana, gas asetilena telah digunakan sebagai pelopor karbon selain daripada metana. Tiga parameter telah dikaji dalam bahagian ini, suhu tindak balas (400 °C - 800 °C), kadar pengaliran pelopor karbon (10-30 sccm) dan tempoh masa tindak balas (5 min-40 min). Semua CNS yang tumbuh dicirikan menggunakan SEM, Mikroskop Penghantaran Elektron (TEM), Analisis Permeteran Graviti Haba (TGA) dan Spektroskopi Raman. Daripada kedua-dua bahagian, tahap prestasi pemangkin nikel tersadur di atas substrat kuprum terhadap pertumbuhan CNS dengan ketumpatan dan kualiti tinggi adalah optimum di atas pemangkin kuprum terelektrosadur nikel yang mempunyai saiz bijian kecil, nipis, meliputi sepenuhnya dan keseragaman tinggi iaitu $1\text{mA}/\text{cm}^2$. Pertumbuhan terus CNS telah berjaya dilaksanakan ke atas pemangkin nikel tersadur pada suhu pertumbuhan yang rendah di mana keadaan CCVD adalah optimum dalam menghasilkan CNS yang berkualiti dan berketumpatan tinggi adalah pada suhu tindakbalas, 600 °C, 40 minit masa tindakbalas dan 30 kepada 100 sccm kadar pengaliran asitilena kepada nitrogen.

GROWTH OF CARBON NANOSTRUCTURE ARRAYS ON NICKEL ELECTROPLATED COPPER SUBSTRATE

ABSTRACT

Since the inventions of CNTs by Iijima in 1991, carbon nanostructure (CNS) in which consists of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) has great attentions among researchers due to the extraordinary properties of this material. A lot of research activities and new findings regarding the potentials of CNS were explored from time to time. One of the potential CNS is it can be used as thermal interface material (TIM) and applied in electronic devices due to high thermal conductivity of this material. Thus, this research is focusing on the synthesis of high quality and density of CNS directly on the platform at low growth temperature towards the potential of CNS for future application as TIM. The first part of this study was the preparation of the heat spreader by electroplating method prior to the growth CNS. Electroplating method was used to coat active metal catalyst, nickel to the copper as substrate and copper was selected as the substrate due to high thermal conductivity of this material whereas nickel is used as the metal due to the ability to grow higher density of CNS and corrosion resistant. Two parameters were studied in this part which was current density (1-30 mA/cm²) and plating time (10 min-60 min). The samples were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX), X-ray Fluorescence (XRF) and Atomic force Microscopy (AFM). For the second part of this study is the growth of CNS via Catalytic Chemical Vapour Deposition (CCVD) where acetylene was used carbon precursor instead of methane. Three parameters were studied for this part, reaction temperature (400 °C - 800 °C), flow rate of acetylene (10-30 sccm) and reaction time (5-40 min). All CNS growth were characterized using SEM,