Synthesis and Characterization of Silicon Carbide Nanotube via Microwave Assisted Method

by

TONY VOO CHUNG SUNG
1531711772

A thesis submitted in fulfilment of the requirements for the degree of Master of Science in Nanomaterials Engineering

Institute of Nano Electronic Engineering
UNIVERSITI MALAYSIA PERLIS (UniMAP)

2018

THESIS DECLARATION FORM

UNIVERSITI MALAYSIA PERLIS

DECLARATION OF THESIS

Author's full name : Tony Voo Chung Sung

Date of birth : 3 March 1991

Title : Microwave Assisted Synthesis of Silicon Carbide Nanotubes

Academic Session : 2015/2016

I hereby declare that this thesis becomes the property of Universiti Malaysia Perlis (UniMAP) and to be placed at the library of UniMAP. This thesis is classified as :

☐ **CONFIDENTIAL** (Contains confidential information under the Official Secret Act 1972)

☐ **RESTICTED** (Contains restricted information as specified by the organization where research was done)

☑ **OPEN ACCESS** I agree that my thesis is to be made immediately available as hard copy or on-line open access (full text)

I, the author, give permission to the UniMAP to reproduce this thesis in whole or in part for the purpose of research or academic exchange only (except during a period of _____ years, if so requested above).

Certified by:

SIGNATURE

SIGNATURE OF SUPERVISOR

910303-12-5461

(NEW IC NO. / PASSPORT NO.)

Dr Voon Chun Hong

NAME OF SUPERVISOR

Date : ________________

Date : ________________

ACKNOWLEDGEMENT

Thanks to God for his blessing and giving me health that enables me to complete my degree of Master of Science in Nano-Material Engineering at University Malaysia Perlis. It is a pleasant aspect that I have now the opportunity to express my gratitude for all of them. It is the most appreciated to honour to my family, my dad and mum which always give an encouragement, motivation, understanding and support over me.

I would like to express thousand my sincere gratitude to my supervisor, Dr Voon Chun Hong and my co-supervisor, Dr Lee Chang Chuan and En Wan Abdul Rahman Assyahid for their invaluable guidance, constant support, and continuous encouragement and help me in all time to carry out this research and writing this thesis. I also sincerely thanks for the time spent on proof reading and correcting my mistakes along with teaching and guiding me in the laboratory.

My special thanks to my examiners who give their comments, opinion and suggestion to improve my research project. I would like to extend my appreciation to all staff of Institute of Nano-Electronic Engineering (INEE) especially to Prof Dr Uda Hashim, Ir. Dr. Mohd Khairuddin Md Arshad, Dr Subash C B Gopinath, Dr Liu Wei Wen, Dr Ruslinda Abdul Rahim and all technical staff from INEE for their special effort with valuable technical guidance during my completion of this project. Special thanks also appreciated for technical staff from School of Material Engineering, En Nasir and En Hadzrul for their helping in my characterization test.

At last but not least, I offer my regards and special thanks for all of my friends who supported and guided me in any aspect during the completion of my study and thus helping me in finishing my thesis.

TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERITURE REVIEW

CHAPTER 3 METHODOLOGY

CHAPTER 4 RESULTS AND DISCUSSION

CHAPTER 5 CONCLUSION

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
2θ	Two-Theta
3D	Three-Dimensional
α-SiC	Alpha-Silicon Carbide
β-SiC	Beta-Silicon Carbide
C	Carbon
CNTs	Carbon nanotubes
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CVD	Chemical Vapor Deposition
d	Distance
DC	Direct Current
D_p	Depth of Penetration
DFT	Density Functional Theory
EDX	Energy Dispersive X-Ray
f	Frequency
FESEM	Field Emission Scanning Electron Microscopy
FeS	Iron (III) Sulphide
FTIR	Fourier Transform Infrared
GaAs	Gallium Arsenic

GHz	Giga Hertz
GPa	Giga Pascals
h	Height
HFCVD	Hot Filament Chemical Vapor Deposition
IR	Infrared
kBr	Potassium Bormide
KHz	Kilo Hertz
kV	Kilo Volt
LaB6	Lanthanum hexaboride
mA	Mili-Amperes
MD	Molecular Dynamics
MgO	Magnesium Oxide
MHz	Mega-Hertz
mm	Milimeters
MMC	Multi-Mode Cavity
MOSFET	Metal–oxide–semiconductor field-effect transistor
ml	Milliliters
MTS	methyltrichlorosilane
MWCNTs	Multi-Walled Carbon Nanotubes
Ni	Nickel
nm	Nano-meters
O	Oxygen
P	Power

PL	Photoluminescence
RF	Radio Frequency
Si	Silicon
SiC	Silicon Carbide
$SiCl_4$	Silica Tetrachloride
Si NW	Silicon Nanowires
SiO	Silicon Monoxide
SiO_2	Silicon Dioxide
SMC	Single-mode Cavity
SMS	Shape Memory Synthesis
SLS	Solution-Liquid-Solid
SiCNTs	Silicon Carbide Nanotubes
SWCNTs	Single-Walled Carbon Nanotubes
TEM	Transmission Electron Microscopy
TGA	Thermo-Gravimetric Analysis
Tan δ	Loss Tangent
VS	Vapor-Solid
VLS	Vapor-Liquid-Solid
W	Watt
XRD	X-Ray Diffraction
°C	Degree Celcius
$\mathcal{E}'$	Dielectric Constant
$\mathcal{E}''$	Dielectric Loss Factor

ε^0	Permeability Free Space
λ	Wavelength
θ	Degree
µg	Micro-gram
µm	Micro-meter
% wt	Weight Percent

LIST OF EQUATIONS

Sintesis dan pencirian tiub nano siliko karbida melalui kaedah berbantu mikro

ABSTRAK

Silikon karbid (SiC) dikenali umum sebagai salah satu bahan paling berguna berdasarkan sifat bahannya yang sangat keras dan menyamai kriteria yang dimiliki oleh berlian. Tiub nano silikon karbida (SiCNTs) dan wayar nano silikon karbida (SiCNWs) mempunyai potensi yang bermanfaat dan stabil pada suhu yang tinggi, dan keadaan persekitaran yang kritikal untuk penggunaan sistem elektronik. Tujuan kajian ini dijalankan adalah untuk mengenalpasti kesan penghasilan nisbah campuran di antara silikon dioksida dan MWCNTs, suhu pemanasan, tempoh pemanasan, dan jenis-jenis nano tiub karbon (MWCNTs dan SWCNTs) pada penghasilan SiCNTs oleh pemanasan menggunakan gelombang mikro dari segi rupa bentuk, komposisi kandungan, sifat-sifat optikal dan kestabilan terma. Kesan nisbah berbeza telah dikaji dengan mevariasikan pelbagai nisbah molar partikel SiO_2 dan MWCNTs dalam adunan 1:1, 1:3, 1:5 dan 1:7 manakala untuk kajian kesan pemanasan pula, suhu telah diubah dari 1350°C, 1400°C dan 1450°C. Tempoh pemanasan selama 20, 40 dan 60 minit telah digunakan dalam kajian ini untuk mengkaji dan mengenalpasti kesan tempoh pemanasan pada penghasilan SiCNTs. Dua jenis CNTs (MWCNTs and SWCNTs) telah digunakan untuk mengkaji kesan perbezaan jenis-jenis CNTs pada penghasilan SiCNMs. Pencampuran ultrasonik digunakan untuk campuran SiO_2 dan MWCNTs dalam ethanol yang kemudiannya dikeringkan sebelum ditekan menjadi 3 mm pellet. Selepas itu, pellet dimasukkan ke dalam mangkuk pijar alumina dan pemanasan gelombang mikro dilakuan dalam 2.45 GHz pelbagai mod rongga gelombang mikro dengan kadar pemanasan 30°C/minit. FESEM dan TEM telah digunakan untuk mengkaji morfologi SiCNMs. Sementara itu, analisis komposisi telah dilakukan dengan menggunakan XRD dan EDX. PL telah digunakan untuk mengkaji sifat-sifat optik manakala, sifat terma telah dikaji dengan menggunakan analisis TGA. Nisbah 1:3 partikel SiO_2 dan MWCNTs menunjukkan penghasilan fasa tunggal SiCNTs fasa disokong oleh corak XRD di mana tiada lagi sisa partikel SiO_2 dan MWCNTs yang dapat diperhatikan. Sementara itu, proses pemanasan pada suhu 1400°C dan tempoh pemanasan 40 minit telah dikenalpasti sebagai suhu dan tempoh paling sesuai untuk penghasilan fasa tunggal SiCNTs di mana partikel SiO_2 dan MWCNTs bertindak balas dengan sepenuhnya menjadi fasa tunggal SiCNTs. Tambahan pula, fasa tunggal SiCNTs telah berjaya dihasilkan daripada campuran partikel SiO_2 dan MWCNTs dalam nisbah 1:3 manakala campuran partikel SiO_2 dan SWCNTs dalam nisbah yang sama membentuk SiCNWs. Imej TEM telah mengesahkan bahawa SiCNTs yang dihasilkan mempunyai struktur tiub berongga manakala SiCNWs mempunyai struktur wayar nano yang kukuh. Ia boleh diandaikan bahawa nisbah partikel SiO_2 dan MWCNTs, suhu dan tempoh pemanasan mempunyai kesan yang signifikan terhadap penghasilan SiCNTs. Selain daripada itu, jenis CNTs juga memainkan peranan yang penting dalam pembentukan SiCNMs di mana SiCNTs telah diperolehi daripada campuran partikel SiO_2 dan MWCNTs manakala SiCNWs telah dihasilkan daripada campuran partikel SiO_2 dan SWCNTs yang telah digunakan. Daripada keputusan kajian ini, dapat disimpulkan bahawa pemanasan gelombang mikro untuk penghasilan fasa tunggal SiCNTs telah dicapai di antara campuran partikel SiO_2 dan MWCNTs pada nisbah 1:3, suhu pemanasan pada 1400°C, tempoh pemanasan selama 40 minit telah digunakan dalam kajian ini.

Microwave Assisted Synthesis of Silicon Carbide Nanotubes

ABSTRACT

Silicon carbide (SiC) is well known as one of the most useful materials due to its high hardness next to diamond. Silicon carbide nanotubes (SiCNTs) and nanowires (SiCNWs) especially have high potential in high temperature and harsh environment electronic applications. The objectives of this study were to investigate the effect of ratio of SiO_2 particles and MWCNTs, heating temperature, heating duration and types of CNTs (MWCNTs and SWCNTs) on the synthesis of SiCNTs by microwave heating in terms of morphology, compositions, optical properties and thermal stability. Effect of different ratio was studied by varying the molar ratio of SiO_2 particles and MWCNTs in the blend to 1:1, 1:3, 1:5 and 1:7 while for the study of effect of heating temperature, temperature was varied from 1350 °C, 1400 °C and 1450 °C. Heating duration of 20, 40 and 60 minutes were used in this study to investigate the effect of heating duration on the synthesis of SiCNTs. Two types of CNTs (MWCNTs and SWCNTs) were used to investigate the effect of type of CNTs on synthesized SiCNMs. Ultrasonic mixing was used to mix SiO_2 particles and MWCNTs in ethanol which was then dried before being cold pressed into 3 mm pellet. After that, the pellet was put into alumina crucible and microwave heating was conducted in a 2.45 GHz multi-mode cavity microwave with heating rate of 30 °C/minute. FESEM and TEM were used to investigate the morphology of the SiCNMs. Meanwhile, composition analysis was done by using XRD and EDX. PL was used to study the optical properties, while thermal properties were investigated by using TGA analysis. Ratio 1:3 of SiO_2 particles and MWCNTs has showed synthesis of single-phase SiCNTs as supported by XRD patterns where no residual of SiO_2 particles and MWCNTs was observed. Meanwhile, heating temperature at 1400 °C and 40 minutes heating duration was determined as the most ideal temperature to synthesize single-phase SiCNTs in which SiO_2 particles and MWCNTs reacted completely become single-phase SiCNTs. Furthermore, single phase SiCNTs was successfully synthesized from blend of SiO_2 particles and MWCNTs in the ratio of 1:3 while blend of SiO_2 particles and SWCNTs in similar ratio formed SiCNWs. Images of TEM have confirmed that the synthesized SiCNTs has hollow tubular structure while SiCNWs has a solid nanowires structure. It can be postulated that ratio of SiO_2 particles and MWCNTs, heating temperature and heating duration has significant effect to the synthesis of SiCNTs. Besides that, type of CNTs (MWCNTs and SWCNTs has significant effect on the formation of SiCNMs where SiCNTs was obtained from the blend of SiO_2 particles and MWCNTs while SiCNWs synthesized when blend of SiO_2 particles and SWCNTs was used. It can be concluded that microwave heating for the synthesis of single-phase SiCNTs was achieved when blend of SiO_2 particles and MWCNTs in the ratio of 1:3, heating temperature at 1400 °C, heating duration of 40 minutes was used in this study.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Silicon carbide (SiC) is an important ceramic material which is known as carborundum and consists of silicon and carbon atom with chemical formula of SiC. The set of unique properties such as high hardness and strength at elevated temperature, excellent thermal conductivity and stability, good wear and corrosion resistance make SiC a highly attractive material for many applications including structural ceramics, heating and corrosion protective elements (Chu *et al.*, 2012; Ivekovic *et al*., 2013). Besides that, SiC is also considered as a high potential candidate for electronic applications such as high power switching and high voltage light emitting diodes (Oliveros, Guiseppi-Elie and Saddow, 2013; Pedersen *et al.*, 2012). Furthermore, high hardness and wear resistance of SiC makes it a very ideal material for abrasive machining applications such as grinding and sand blasting (Wijesundara and Azevedo, 2011).

Due to the discovery of carbon nanotubes (CNTs), nano-materials has been thoroughly studied and investigated worldwide by researchers due to the novel properties which are associated with large surface area and quantum size effects. For example, when an object is in nano-scale size, its surface area to volume ratio is high (Huang *et al.*, 2013). This in turn increases the reactivity due to more surfaces are available for reactions. Meanwhile, quantum size effect describes the physics of electron properties in solids when particle size falls within nano-scale size (Aznan and Johan, 2012). Changes of electron properties at nano-size caused the changes in the properties of bulk material. These novel properties of nano-materials show new and unsual properties which render a limitless possibility of potential applications for nano-materials in many fields including medicine, composite, structural, aerospace and others (Dumrongbunditkul *et al*., 2016; Kim *et al*., 2016; Qu *et al.*, 2016). Nano-materials are materials that consisted of nano-scale dimensions within range of 1-100 nm and produced by nanotechnology.

Meanwhile, nanotechnology is a branch of technology that deals with dimensions of materials of less than 100 nm especially in manipulation of individual atoms and molecules (Kim *et al.*, 2016). In brief, nano-materials can be categorized into zero-dimensional (0 D), one-dimensional (1 D), two-dimensional (2 D) and three-dimensional (3 D) with each has different dimensions over nanometer length. 0 D nano-materials are structures with all dimensions on nanometer scale such as nano-particles and nano-spheres (Yu *et al*., 2015), while 1 D nano-materials are structures with two dimensions on nanometer scale such as nanowires and nanotubes (Suresh 2013). 2 D nano-materials only have one dimension on the nanometer scale that is perpendicular to layer plane such as nano-flakes and nano-platelets (Zhang, 2015). 3 D nano-materials are ensembles of the nano-materials such nanowires connected through single-crystalline junctions and have overall dimensions on the nano or micro scale (Wu *et al.*, 2015).

Among SiC nanostructures, one dimensional SiC nanostructures such as SiC nanowires, nanotubes, nano-rods, nano-whiskers and many others have been extensively studied by researchers due to the potential of one dimensional SiC nanostructures in wide range of applications. Many one-dimensional SiC nanostructures has been reported successfully applied in applications such as photo-catalyst (Liu *et al*., 2012), field-effect transistor (Andersson, Pearce and Lloyd, 2013), composite (Pozuelo, Kao and Yang, 2013), field emitters (Wu *et al.*, 2012), sensors (Wang *et al*., 2012), catalyst (Hao *et al*., 2012), super-capacitors (Gu *et al.*, 2013) and bio-imaging probes (Fradetal *et al.*, 2014) due to the outstanding properties exhibited by one dimensional SiC nanostructures such as high thermal conductivity, excellent chemical inertness, high energy band gaps and better field emitting properties (Mizsei and Czett, 2012; Xin *et al.*, 2012)

Silicon carbide nanotubes (SiCNTs) are known as one of the many types of one dimensional SiC nanostructures which has the structure of nanotube consisted tubular layer with silicon and carbon atoms joined in strong covalent bonding (Taguchi *et al*., 2005). SiCNTs are extensively studied since SiCNTs have properties such as high reactivity of exterior surface and excellent stability at high temperature, high fracture toughness, excellent thermal stability and ability to withstand high temperature and corrosive environments comparing to CNTs (Barghi, Tsotsis and Sahimi, 2014).

1.2 Problem Statement

Although SiCNTs was successfully synthesized at low temperature of 935°C from the reaction of CNTs and SiO powder by Sun *et al.*, (2002), Latu-Romain *et al.*, (2013) from the SiNW and Xie, Tao and Wang (2007) by CVD method, the cost SiO powder used in the reaction was expensive compared to SiO_2 particles. Furthermore, the synthesized SiCNTs also consisted of unreacted SiO powder and CNTs and thus single-phase SiCNTs could not be obtained. Meanwhile, use of the gold catalyst and HFCVD by Latu-Romain *et al.,* (2013) was practically impossible and rendered very high cost for the synthesis of SiCNTs. Moreover, use of the catalyst during the synthesis of SiCNTs by CVD method often caused the presence of impurities and this resulted in the need of further purification steps to remove the impurities. In addition, the use of methyltrichlorosilane (MTS) as precursor was expensive and costly compared to CNTs. All of these, in turn caused the increase of production costs of SiCNTs.

Based on these reported current methods of synthesis of SiCNTs, there are disadvantages for the methods such as large consumption of energy, long heating duration, lower heating rates and presence of impurities which has resulted difficulties to obtain high purity single-phase SiCNTs with reduced processing times and high heating rates. Thus, there is need to propose an alternative synthesis method which can reduce the consumption of energy and synthesize high purity single-phase SiCNTs with shorter heating duration and fast heating rates.

Recently, microwave heating method has been developed as the new way for the synthesis of the SiC nanostructures such as nano-powder (Ebadzadeh and Marzban-Rad, 2009; Moshtaghioun *et al*., 2012; Van Laar *et al*., 2015), nano-wires (Lu *et al.*, 2007; Oh *et al*., 2011; Sundaresan *et al.*, 2007) and nano-whiskers (Kuang and Cao, 2013; Li, Shirai and Fuji, 2013). The first successful synthesis of SiC from silicon and charcoal powder by using commercial microwave oven at 2.45 GHz for 10 minutes was reported at 1994, although impurity was observed together with the synthesized SiC. Microwave is a form of electromagnetic energy with frequency range of 300 MHz to 300 GHz and is widely used in telecommunications. Microwave heating is the process in which the material absorbs electromagnetic energy of microwave via molecular-level interactions with electromagnetic field (Santos *et al*., 2011). Materials with high dielectric properties and polar characteristics such as water and carbon are able to interact with the electromagnetic field of microwave and thus volumetrically produce heat energy (Yu, Shrestha and Baik, 2015).

Comparatively, conventional heating involves the transfer of the heat from heat sources to the material through the mechanism of conduction, convection and radiation. Conventional methods possess some disadvantages since the heat loss to surroundings frequently occurs during the transfer of the heat from heat source to materials. Furthermore, the heating rate and distribution of heat inside the material are not uniform because of the instability in the heat transfer and difference in the gradient of the temperature from outside to inside of material (Oghbaei and Mirzaee, 2010). Meanwhile, microwave heating is able to synthesize the SiC nanostructures with no impurities and chemical catalyst is not necessary. Furthermore, microwave heating has shown that faster heating rate, shorter heating duration and lower consumption of energy can be achieved for the synthesis of SiC nanostructures (Wang *et al.*, 2016).

Carbon materials such as multi-walled carbon nanotube (MWCNTs) and single-walled carbon nanotubes (SWCNTs) were known as good microwave absorbing materials and can be heated uniformly and rapidly when exposed to microwave heating (Kim, Lee and Lee, 2014). By using the advantages of interaction of CNTs with microwave, a fundamental study of synthesis of SiCNTs by using microwave assisted synthesis was proposed.

1.3 Research Objective

This study focused on the feasibility of synthesis of SiCNTs by using microwave heating and the effect of processing parameters on the formation of SiCNTs. The objectives of this study are:

a) To investigate the effect of molar ratio of SiO_2:MWCNTs, heating temperature and heating duration on the formation of SiCNTs by microwave heating in terms of morphology, compositions, optical and thermal properties

b) To investigate the effect of types of CNTs (MWCNTs and SWCNTs) on the formation of SiCNTs by microwave heating in terms of morphology, compositions, optical and thermal properties.