

Parameter optimization of CNT production using Sri Lankan graphite by arc discharge method

Rathnayake Mudiyanseelage Sunanda Jayalath Gunasekara
(R. M. S. J. Gunasekara)

(09/8110)

Degree of Master of Philosophy



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

Department of Electrical Engineering

University of Moratuwa

Sri Lanka

December 2012

**Parameter optimization of multi wall carbon nano tube
production (MWCNT) using Sri Lankan graphite by electric
arc discharge method**

Rathnayake Mudiyanseelage Sunanda Jayalath Gunasekara
(R. M. S. J. Gunasekara)

(09/8110)

Degree of Master of Philosophy



University of Moratuwa, Sri Lanka.
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

Department of Electrical Engineering

University of Moratuwa

Sri Lanka

December 2012

DECLARATION

I declare that this is my own work and this thesis does not contain any material previously submitted for a Degree or Diploma in any other University or published elsewhere, without acknowledgement to the best of my knowledge.

Also, I hereby grant to University of Moratuwa the non-exclusive right to reproduce and distribute my thesis, in whole or in part in print, electronic or any other medium. I retain the right to use this content in whole or part in future works (such as articles or books).

.....

R. M. S. J. Gunasekara

Date:

The above candidate has carried out research for the M. Phil thesis under our supervision.



University of Moratuwa, Sri Lanka
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

.....

Prof. J. P. Karunadasa

Date:

Supervisor

.....

Prof. Ajith de Alwis

Date:

Supervisor

.....

Dr. Lilantha Samaranayake

Date:

Supervisor

ACKNOWLEDGEMENT

I acknowledge with gratitude the Sri Lanka Institute of Nanotechnology (SLINTEC) for giving me the opportunity to conduct this project with full financial support along with National Science Foundation while providing the access for its valuable high end equipment facilities.

I am grateful to Prof. J.P. Karunadsa, Prof. Ajith de Alwis and Dr. Lilantha Samaranayake, my supervisors who very generously spent their precious time to provide necessary guidance and assistance to carry out this task.

I also extend my gratitude and thank to Prof. Veranja Karuinanayake, Science Team Leader, Sri Lanka Institute of Nanotechnology and Prof. Gehan Amarathunge, Department of Electrical Engineering, University of Cambridge and Head of Research and Innovations at SLINTEC, providing me with all necessary guidance in carrying out this project.

Further I wish to sincerely thank Dr. Nilwala Kottegoda, Dr. Gamini Kumarasinghe and Dr. Jeewantha Premachandra at SLINTEC who helped me in numerous ways to complete my project successfully.

I am also thankful to all my colleagues at SLINTEC for encouragement and assistance extended to me, especially to Mr. Neil who has assisted me in preparation of arc discharge set up.

R. M. Sunanda Jayalath Gunasekara

ABSTRACT

Since their discovery in 1991 by Iijima, carbon nanotubes have been of great interest. The key advantages of these structures are their electronic, mechanical, optical and chemical characteristics, which open a way to a variety of applications. These properties can even be measured on single nanotubes. For commercial application, large quantities of purified nanotubes are needed.

Different types of carbon nanotubes can be produced in various ways. The most common techniques used nowadays are: arc discharge, laser ablation, chemical vapor deposition and flame synthesis.

Fundamental and practical nanotube researches have shown possible applications in the fields of energy storage, molecular electronics, nano-mechanical devices, and composite materials. Real applications are still under development.

This project is basically focused on arc discharge method of CNT production using Sri Lankan vein graphite. Sri Lankan graphite is unique due to its perfect crystalline structure and the higher as mined purity compared with that of commonly available flake graphite. This type of natural resource is found mainly in Sri Lanka. Detailed study on flake and vein graphite was carried out in this study as one of its objectives. Also SEM and TGA analysis of the multiwall carbon nanotubes are discussed. Special technique for comparing diameters of multiwall wall carbon nanotube was developed by using TGA. Further, the cross section analysis was carried out for the arc sputter to analyze the formation of the nanotubes on the cathode. Another objective here was to identify the optimum parameters for the production of CNT using the arc discharge method. Arcing time, current, chamber inert gas, chamber pressure and the type of the electrode were the variables. Arcing current around 100 A, pressure around 700~900Torr and arcing duration around 60s with helium as the inert gas were the optimized conditions.

Key words: Vein Graphite, CNT, MWCNT, Arc discharge, Nanotube

TABLE OF CONTENTS

DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT.....	iii
TABLE OF CONTENTS.....	iv
TABLE OF FIGURES	vii
LIST OF TABLES	xi
LIST OF ABBREVIATIONS	xii
Chapter 1 : INTRODUCTION.....	1
1.1 Background.....	1
1.1 Structure of CNT.....	2
1.2 Research objectives.....	3
Chapter 2 : LITERATURE STUDY	4
2.1 Different Structures of Carbon Nanotubes.....	4
2.1.1 Single Wall Carbon Nano Tubes (SWCNT).....	4
2.1.2 Multi Wall Carbon Nanotube (MWCNT).....	6
2.2 Physical Properties of CNT.....	8
2.2.1 Strength	8
2.2.2 Hardness.....	9
2.2.3 Kinetic.....	9
2.2.4 Electrical	10
2.2.1 Thermal	11
2.3 Applications of carbon nanotubes	11
2.3 Manufacturing of carbon nanotubes.....	12
2.4 Global trend for carbon nanotube.....	14
2.7 Introduction to graphite.....	18

2.7.1 Application of natural graphite	21
Chapter 3 : MATERIALS AND METHODS	23
3.1 Characterization techniques	23
3.1.1 Thermo gravimetric analysis (TGA).....	23
3.1.2 Scanning electron microscopy (SEM)	25
3.1.3. Atomic force microscopy (AFM)	27
3.1.4 Elemental analysis	28
3.2. Other equipment used	28
3.2.1 Vacuum pump	28
3.2.2 High current DC power supply	28
3.2.3 High voltage generator.....	29
3.2.4 Stop watch.....	29
3.2.5 Glove box.....	29
3.3 Methodologies.....	29
3.3.1 Characterization of raw materials	29
3.3.2 Characterization of standard CNT samples	32
3.2.3 Experiments with commercial grade CNT.....	32
3.2.4 Setting up of the arc discharge apparatus	33
3.2.5 Cross section analysis of the arc soot	38
3.2.6 Testing with different arcing times	38
3.2.7 Testing with different arcing current	39
3.2.8 Testing with different arcing environment pressure	40
3.2.9 Testing with different arcing environment.....	40
3.2.10 Testing with an external electrical field.....	42
3.2.11 Testing with different shapes and materials of anode/cathode	43
3.2.12 Testing with Flake graphite anode and cathode.....	43
Chapter 4 : RESULTS AND DISCUSSIONS	44
4.1 Characterization of raw materials	44
4.2 Characterization of standard CNT samples	47
4.3 Experiments with commercial grade CNT	50

4.4 Setting up the arc discharge apparatus	53
4.5 Cross section analysis of the arc soot.....	53
4.6 Testing with different arcing time.....	55
4.7 Testing with different arcing currents	58
4.8 Testing with different arcing environment pressures.....	64
4.9 Testing under different arcing environments	68
4.10 Testing with an external electric field.....	74
4.11 Testing with different shapes and materials of anode/cathode	75
Chapter 5 : CONCLUSIONS	78
5.1 Future works	79
References	80



University of Moratuwa, Sri Lanka
Electronic Theses & Dissertations
www.lib.mrt.ac.lk

TABLE OF FIGURES

Figure 1-1 Schematic illustration of the basal and edge planes in graphite (7)	3
Figure 2-1 SWCNT (Original is in colour)	4
Figure 2-2 SWNTs with different chiralities.	4
Figure 2-3 Chiral Vectors of SWCNT (10) original is in colour	6
Figure 2-4: MWCNT(Original is in colour)- Generated from NINITHI software	6
Figure 2-5: Different structures of MWCNT- TEM images.....	7
Figure 2-6 Chiral notation of SWCNT (10)- original is in colour	10
Figure 2-7 Application of MWCNT	12
Figure 2-8 Schematic drawings of the laser ablation apparatus (8).....	13
Figure 2-9 Schematic diagram of synthesis of CNT by CVD technique.....	13
Figure 2-10 Comparison of CNT, Graphene and Fullerene (Original is in colour) publication [20].....	14
Figure 2-11 Productivity of Nanotubes.....	16
Figure 2-12 commercial scale CNT manufactures (Original is in colour)	17
Figure-2-13 Different form so Carbon (Original is in colour).....	18
Figure 2-14 sp ³ -hybrid orbital	19
Figure 2-15 sp ² Hybridization	19
Figure 2-16 Band structure of graphite	20
Figure 2-17 Lattice Structure of Graphite.....	21
Figure 3-1 Schematic diagram of TGA (Original is in colour) (www.tainstruments.com).....	23
Figure 3-2 Typical Schematic diagram of a SEM set-up.....	26
Figure 3-3 An AFM probe scans over a sample surface (Original is in colour).....	27
Figure 3-4 TGA Analysis example	31
Figure 3-5 Weight % calculation from DTG curve (Sample: CNT produced with arc discharge)	32
Figure 3-6 First generation arcing setup in open air(Original is in colour)	34
Figure 3-7 schematic view of the arc-discharge apparatus (26)	34
Figure 3-8 Second generation arc discharge set up (Original is in colour).....	35

Figure 3-9 Third generation arc discharge setup(Original is in colour)	36
Figure 3-10 Final Arc discharge set up(Original is in colour).....	37
Figure 3-11 Arcing inside de ionized water. (Original is in colour).....	41
Figure 3-12 Schematic diagram of set up with external electric field	42
Figure 4-1 - SEM images of (A) Flake graphite, (B) Vein Graphite	44
Figure 4-2 XRD Analysis of Vein and Flake graphite	44
Figure 4-3 TGA results of Vein graphite (solid line) and Flake graphite (Dotted line) (Original is in colour)	46
Figure 4-4 SEM image of Standard MWCNT from Sigma with 13000 magnification.....	47
Figure 4-5 SEM image of Standard MWCNT from Sigma with 60000 magnification.....	48
Figure 4-6 TGA Analysis of Sigma MWCNT (solid line) and Sigma SWCNT (dash line) (Original is in colour).....	49
Figure 4-7 AFM analysis of MWCNT(Original is in colour).....	50
Figure 4-8 TGA analysis of commercial MWCNT samples (Original is in colour)	50
Figure 4-9 Repeat TGA analysis of commercial grade MWCNT samples (Original is in colour).....	52
Figure 4-10 Temperature at maximum decomposition rate or the maximum heat flow while decomposing of the CNT Vs CNT Diameter for commercial samples (Original is in colour)	52
Figure 4-11 SEM image of Cross section of the Arc soot (Original is in colour)	53
Figure 4-12 SEM image of the arc soot A) view from the top B) image of the middle structure c) image of the formed CNT layer D) view of the bottom surface	54
Figure 4-13 SEM images of the cathode deposit for arc time of 10s, 15s, 20s and 25s	55
Figure 4-14 SEM images of the cathode deposit for arc time of 30s, 40s, 45s and 50s	55
Figure 4-15 SEM images of the cathode deposit for arc time of 55 s, 60s, 90s and 120 s	56

Figure 4-16 Temperature at the maximum decomposition of the samples with different arcing time (Original is in colour).....	57
Figure 4-17 CNT yield of the samples with different arcing times (Original is in colour)	58
Figure 4-18 Temperature at the maximum decomposition rate vs arcing time	59
Figure 4-19 CNT yield vs. arcing current (Original is in colour).....	60
Figure 4-20 CNT yield % vs. arcing current (Repeat experiment) (Original is in colour)	61
Figure 4-21 CNT yield vs. arcing current (Repeat test) (Original is in colour).....	61
Figure 4-22 Temperature at the maximum decomposition rate vs .arcing current (Repeat experiment) (Original is in colour).....	62
Figure 4-23 SEM images of CNTs produced with different arcing current (60A, 88 A, 92 A, 100A)	63
Figure 4-24 SEM images of CNTs produced with different arcing current (100A and 110A).....	63
Figure 4-25 SEM images of CNTs produced with different arcing current (100A and 118A).....	64
Figure 4-26 CNT yield Vs. Arcing pressure (Original is in colour).....	66
Figure 4-27 temperature at the maximum decomposition rate vs. arcing environment pressure (Original is in colour)	66
Figure 4-28 SEM images of produced CNT for different arcing pressure	67
Figure 4-29 SEM images of produced CNT for different arcing pressure	67
Figure 4-30 TGA analysis of the sample with N2 at 1 atm, 100 A (Original is in colour)	68
Figure 4-31 TGA analysis of the sample with N2 at 900Torr, 100 A	69
Figure 4-32 TGA results of the test with He gas (Solid line: 900Torr, 100A, 60s Dash line : 1 atm, 100A, 60s) (Original is in colour)	69
Figure 4-33 CNT Yield with different gases	70
Figure 4-34 SEM images of the CNT produced with Nitrogen as the inert gas	70
Figure 4-35 SEM images of the CNT produced with Argon as the inert gas	71
Figure 4-36 SEM images of the CNT produced with Helium as the inert gas	71
Figure 4-37 Comparison of SEM images of arc with He (left) and N2 (Right)	72

Figure 4-38 Carbon onion formation on the CNT produced with nitrogen gas as the inert media.....	72
Figure 4-39 Clean CNT formation with He	73
Figure 4-40 SEM images of the samples from arcing inside water	74
Figure 4-41 SEM images of the HV (high voltage) and LV (low voltage) cathode deposits of the test with an external electric field.....	75
Figure 4-42 SEM image of the cathode deposit of the copper cathode	76
Figure 4-43Cathode deposit of Flake test - image 1	77
Figure 4-44Cathode deposit of Flake test - image 2	77
Figure 5-1 Comparison of the standard Sigma CNT vs produced CNT	78



LIST OF TABLES

Table 2-1 Comparison of mechanical properties of CNT	9
Table 2-2 Top ten authors for CNT related publications (20)	15
Table 2-3 Top ten institute for CNT related publications (20)	16
Table 3-1 Specification of the commercial grade CNTs used for the analysis.....	33
Table 3-2 Description of the samples for different arcing time	38
Table 3-3 Sample description for the samples with different arcing currents	39
Table 3-4 Sample description for the samples with different arcing current by using forth arcing set up	39
Table 3-5 Sample description for the samples with different arcing environment pressure by using forth arc discharge set up.....	40
Table 3-6 : Sample description for the samples with different arcing environment..	41
Table 4-1 Elemental analysis of vein graphite.....	45
Table 4-2 Elemental Analysis of Flake Graphite.....	45
Table 4-3 Temperatures at maximum decomposing rate of commercial MWCNT samples	51
Table 4-4 TGA results of the samples with different arcing time	56
Table 4-5 Results of the test with different arcing currents by using the second set up.....	59
Table 4-6 TGA results of the sample produced by varying the current (repeat)	60
Table 4-7 Temperature at the maximum decomposition rate and the CNT yield for the samples with different arcing environment pressure (taken from TGA results)	65

LIST OF ABBREVIATIONS

<u>Abbreviation</u>	<u>Description</u>
Å	Angstrom
AFM	Atomic Force Microscope
Ar	Argon
CNT	Carbon nanotube
EDX	Energy Dispersive X-ray analysis
FTIR	Fourier Transform Infrared Spectroscopy
g	gram
kg	kilogram
kV	Kilo Volts
MWCNT	Multi wall carbon nanotube
SEM	Scanning Electron Microscope
SWCNT	Single wall carbon nanotube
TGA	Thermo Gravimetric Analysis
CVD	Chemical Vapor deposition
DC	Direct current
USA	United States of America
DWCNT	Double wall carbon nanotube
VPGCF	Vapor phase grown carbon fibers



University of Sri Lanka
Electronic Theses & Dissertations
United States of America