



UNIVERSITI PUTRA MALAYSIA

**ELECTRICAL CHARACTERIZATION OF CARBON NANOTUBE AS GAS SENSING
ELEMENT**

FARAH ANIZA MOHD YUSOF

T FK 2007 45



**ELECTRICAL CHARACTERIZATION OF
CARBON NANOTUBE AS GAS SENSING
ELEMENT**

FARAH ANIZA MOHD YUSOF

**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

2007



**ELECTRICAL CHARACTERIZATION OF CARBON NANOTUBE AS GAS
SENSING ELEMENT**

By

FARAH ANIZA MOHD YUSOF

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirement for the Degree of Master of Science**

June 2007



This work is dedicated to

My beloved husband, Ahmad Syakir Abdul Rashid

My father and mother,

Mohd Yusof Hj. Ahmad and Siti Rohani Hj. Khulan

And my brother and sister,

Farid Azwan Mohd Yusof and Farah Emalina Mohd Yusof

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

ELECTRICAL CHARACTERIZATION OF CARBON NANOTUBE AS GAS SENSING ELEMENT

By

FARAH ANIZA MOHD YUSOF

June 2007

Chairman: Roslina Mohd Sidek, PhD.

Faculty: Engineering

Gas sensing is very important in order to detect dangerous gases like carbon dioxide, ammonia and acetylene, which are commonly used in industries as well as in medical applications. Carbon Nanotube is a promising candidate for gas sensing element because of their large surface area. Therefore, they offer excellent sensitivity and rapid response towards surface changes.

This work aims to investigate carbon nanotubes as gas sensing element. The growth of carbon nanotube has been done using Chemical Vapor Deposition (CVD) technique. The physical and electrical characteristics of carbon nanotube have been characterized using microscopes and source measurement unit. Sensors were fabricated and the variations of electrical resistance upon the exposure of carbon dioxide, ammonia and acetylene gas have been investigated.

The technique for growing carbon nanotubes that is called Floating Catalyst CVD has been used to produce grams of carbon nanotube. The temperature was set from

800°C to 900°C. For that range of temperature, grams of carbon nanotubes are produced in which the diameter is from 40 nm – 200nm and the length is in micrometer. The carbon nanotubes produced are found to have multi-layered wall in about 8nm thickness. The diameter, length and wall thickness have been measured using the Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and Transmission Electron Microscope (TEM). The multi-layered wall indicates that the carbon nanotubes are Multi-Walled Carbon Nanotubes (MWNTs).

Gas-sensing samples have been prepared in the forms of pellet and films. Upon exposure of carbon dioxide, ammonia and acetylene gas, the resistance of the samples increases from their steady state value. From the research, it was found that the sensor is sensitive to carbon dioxide, ammonia and acetylene gas. The sensor can be operated at room temperature with response time as fast as 0.1 to 1 second.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**GAMBARAN SIFAT ELEKTRIK KARBON NANOTIUB SEBAGAI
ELEMEN PENDERIA GAS**

Oleh

FARAH ANIZA MOHD YUSOF

Jun 2007

Pengerusi: Roslina Mohd Sidek, PhD.

Fakulti: Kejuruteraan

Penderia gas penting untuk mengesan gas-gas yang bahaya seperti karbon dioksida, amonia dan asetilena yang selalu digunakan dalam industri dan juga perubatan. Karbon Nanotub adalah bahan yang berpotensi sebagai elemen penderia gas kerana mempunyai luas permukaan yang besar.

Kajian ini berhasrat untuk mengkaji karbon nanotub sebagai elemen penderia gas. Penghasilan karbon nanotub dilakukan menggunakan teknik Pemendapan Wap Kimia (CVD). Ciri-ciri fizikal dan elektrik karbon nanotub dikaji menggunakan beberapa jenis mikroskop dan unit ukuran. Sampel disediakan dan perubahan rintangan elektrik terhadap pendedahan gas karbon dioksida, amonia dan astilena telah dikaji.

Teknik untuk menghasilkan karbon nanotub iaitu Pemendapan Wap Kimia bermangkin terapung (FCCVD) digunakan untuk penghasilan karbon nanotub dalam kuantiti gram yang banyak. Suhu yang digunakan adalah dari 800°C – 900°C.

Untuk suhu sebegini, karbon nanotub dihasilkan dalam beberapa gram yang mempunyai diameter dari 40 nm – 200nm dan panjang dalam ukuran mikron. Karbon nanotub yang terhasil mempunyai dinding berlapis setebal 8nm. Diameter, panjang dan ketebalan dinding diukur menggunakan Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) dan Transmission Electron Microscope (TEM). Dinding karbon nanotub yang berlapis menunjukkan ia adalah jenis Karbon Nanotub Dinding Berlapis (MWNTs).

Sampel penerima gas telah disediakan dalam bentuk pelet dan filem. Semasa pendedahan kepada gas karbon dioksida, amonia dan asetilena, rintangan sampel adalah lebih tinggi dari nilai rintangan asal tanpa gas. Berdasarkan kepada kajian ini mendapati bahawa penerima adalah sensitif terhadap gas karbon dioksida, amonia dan asetilena. Penerima ini boleh beroperasi pada suhu bilik dengan masa respon 0.1 ke 1 saat.

ACKNOWLEDGEMENTS

The first and foremost, I am sincerely thankful to Allah the Almighty for giving me the chance to complete my research project in time. With His blessing, I admit that I had managed a good time to accomplish such work that may give benefits to others soon.

This project had been done with the assistance of many persons. On the top of my mind would be my main supervisor, Dr. Roslina Mohd Sidek for the nonstop guidance during this project. Also, this gratefulness goes to other members of supervisory committee, Dr. Syed Javaid Iqbal and Prof. Dr. Fakhru'l Razi Ahmadun for their technical supports and suggestions that they had given to me.

I would also like to give thousand appreciations to my colleagues, Faizah Md. Yasin, Nazlia Girun, Muataz Ali Atieh and Wan Suhaimizan for all the technical help and leisure discussions throughout this project.

Last but not least, my gratitude goes to my understanding and supporting husband and my parents who have continuously given support to drive me forward. Thank you very much all!

I certify that an Examination Committee has met on 5th June 2007 to conduct the final examination of Farah Aniza Mohd Yusof on her Master of Science thesis entitled “Electrical Characterization of Carbon Nanotube As Gas Sensing Element” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the degree of Master of Science.

Members of the Examination Committee are as follows:

Abdul Halim Shaari, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Suraya Abdul Rashid, PhD

Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Sudhanshu Shekar Jamuar, PhD

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Razali Ismail, Ph.D.

Associate Professor
Faculty of Electrical Engineering
Universiti Teknologi Malaysia
(External Examiner)

HASANAH MOHD GHAZALI, PhD

Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 24 October 2007

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Roslina Mohd Sidek, PhD

Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Syed Javid Iqbal, PhD

Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Fakhru'l-Razi Ahmadun, PhD

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

AINI IDERIS, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 15 November 2007

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

FARAH ANIZA MOHD YUSOF

Date: 13 September 2007

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGEMENTS	vii
APPROVAL	viii
DECLARATION	x
LIST OF TABLES	xiv
LIST OF FIGURES	xv
LIST OF ABBREVIATIONS	xix
CHAPTER	
1 INTRODUCTION	1
1.1 Nanotechnology	1
1.2 Gas Sensing Element	2
1.3 Problem Statement	3
1.4 Aims and Objectives	4
1.5 Scope of Study	4
1.6 Thesis Layout	5
2 LITERATURE REVIEW	7
2.1 Carbon Nanotubes and Its Properties	7
2.1.1 Structure and Physical Appearance of Carbon Nanotubes	8
2.1.2 Types of Carbon Nanotubes	12
2.1.3 Atomic Structure and Energy Spectrum	13
2.1.4 Mechanical, Thermal and Electrical Properties	14
2.2 Growth Methods	24
2.2.1 Arc-Discharge	25
2.2.2 Laser Ablation	26
2.2.3 Chemical Vapor Deposition (CVD)	28
2.3 Characterization Methods of the Carbon Nanotubes	31
2.3.1 Atomic Force Microscope (AFM)	32
2.3.2 Scanning Electron Microscopy (SEM)	35
2.3.3 Transmission Electron Microscopy (TEM)	35
2.4 Application of Carbon Nanotubes	36
2.4.1 Electronic Applications	37
2.4.2 Mechanical Applications	38
2.4.3 Chemical Applications	38
2.4.4 Biomedical Applications	39
2.5 Carbon Nanotube-Based Gas Sensor	39
2.5.1 Types of Sensors's Design using Carbon Nanotubes	41
2.5.2 Types of Gases	44
2.5.2.1 Oxidizing Gas	44
2.5.2.2 Reducing Gas	45
2.5.3 Gas Sensing Characterization	48

	2.5.4	Response Time	49
	2.5.5	Sensitivity	49
	2.6	Summary	51
3		METHODOLOGY	52
	3.1	Carbon Nanotubes Growth with Chemical Vapor Deposition (CVD) Method	52
	3.1.1	Conditions for CVD	54
		3.1.1.1 Reaction Temperature	54
		3.1.1.2 Hydrogen Flow Rate (HRF)	55
		3.1.1.3 Reaction Time	56
	3.1.2	Running the Experiment	56
	3.2	Imaging the Carbon Nanotubes	57
	3.2.1	Atomic Force Microscopy (AFM)	58
	3.2.2	Scanning Electron Microscopy (SEM)	61
	3.2.3	Transmission Electron Microscopy (TEM)	63
	3.3	Current-Voltage Measurement	66
	3.3.1	Using Atomic Force Microscope	66
	3.3.2	Using Source-Measurement Unit (SMU)	67
	3.4	Impedance Analysis	70
	3.4.1	Sample Preparation	71
	3.4.2	Measurement Implementation	72
	3.5	Gas Sensor Development	74
	3.5.1	Experimental Setup	74
4		RESULTS AND DISCUSSION	76
	4.1	Characterization of Carbon Nanotubes	76
	4.1.1	Scanning Electron Microscopy (SEM) Characterization	77
	4.1.2	Atomic Force Microscopy (AFM) Characterization	79
	4.1.3	Transmission Electron Microscopy (TEM) Characterization	80
	4.2	Current-Voltage Measurement	83
	4.2.1	Using Atomic Force Microscopy (AFM)	83
	4.2.2	Using Source-Measurement Unit (SMU)	84
	4.3	Impedance Analysis	89
	4.4	Gas-Sensing Element Characteristics	92
	4.4.1	Effect on Resistance upon Exposure of Carbon Dioxide Gas	94
	4.4.2	Effect on Resistance upon Exposure of Ammonia Gas	97
	4.4.3	Effect on Resistance upon Exposure of Acetylene Gas	101
	4.4.4	Reproducibility of Sensors	104
	4.4.5	Response Time	106
	4.4.6	Sensitivity of Gas-Sensing Element	107
5		CONCLUSIONS AND RECOMMENDATIONS	110
	5.1	Conclusion	110
	5.2	Contribution of Study	111

5.3	Limitation of Study	111
5.4	Further Development and Challenge	111
REFERENCES		113
APPENDICES		119
BIODATA OF THE AUTHOR		127
LIST OF PUBLICATIONS		128

LIST OF TABLES

Table		Page
2.1	Structures and Chirality	12
2.2	Carbon Nanotubes Classifications	13
2.3	Electrical and Mechanical Characteristics of Carbon Nanotubes	15
3.1	Condition Parameter in CVD Technique	54
3.2	Sample Specifications	71
4.1	Diameter and Wall Thickness	81
4.2	Resistance, Resistivity and Conductivity for Pellet and Films Sample Using Source-Measurement Unit (SMU)	87
4.3	Properties of Carbon Nanotubes Using Atomic Force Microscope (AFM)	88
4.4	Impedance Analysis	91
4.5	Recovery Time After gas Exposure	106
4.6	Sensitivity of Sensor upon Gas Exposure	107
4.7	Comparison of Sensor Performance upon Gas Ammonia	108
4.8	Comparison of Sensor Performance upon Gas Carbon Dioxide	109

LIST OF FIGURES

Figure		Page
2.1	SEM Micrograph of a Bare SWNT Rope [Pammi, 2003]	8
2.2	Structures of Carbon Nanotubes, a) An armchair nanotube, b) A zig-zag nanotube and (c) A chiral nanotube. The diameter of the nanotubes depends on the values of n and m [Pammi, 2003]	9
2.3	Chiral Vector and Chiral Angle of Folding of Graphene Sheet	10
2.4	Chiral Vector That Form Metallic or Semiconducting CNTs [Pammi, 2003]	11
2.5	Schematic Diagram of the Electron Transverse Transport within One MWNT [Yang et al., 2004]	19
2.6	a) Electrical Measurement in Longitudinal Direction [Yang et al., 2004]	21
2.6	b) Electrical Measurement in Transverse Direction [Yang et al., 2004]	21
2.7	I-V Curves for 40 μ m Carbon Nanotubes Sample in Parallel and Perpendicular Direction [Yang et al., 2004]	22
2.8	Relationship between Electrical Resistance and Thickness of MWNT Films [Yang et al., 2004]	22
2.9	An Illustrated Measured Impedance Spectrum of Sensor [Yang et al., 2004]	24
2.10	Schematic Diagram of CNT Formation Apparatus by Arc-Discharge Method	25
2.11	Laser Ablation Configuration	27
2.12	Chemical Vapor Deposition Apparatus	29
2.13	Image scanning by AFM [Wesedanger et al., 1994]	34
2.14	Photographs of Sensors Produced by Connecting Two Metal Electrodes Using Silver Adhesive Paint on Compressed Pellets [Villalpando-Paez et al., 2004]	43

2.15	Photographs of Sensors Produced by Connecting Two Metal Electrodes Using Silver Adhesive Paint on Films of CN _x Nanotubes [Villalpando-Paez et al., 2004]	43
2.16	Sensor Response on NO ₂ Gas at Different Temperature and NO ₂ Concentrations [Cantalini et al., 2004]	45
2.17	Transient Resistance Change of the Sensor Upon Exposure to 10 ppm Ammonia Gas at Operating Temperature of 330°C [Yun et al., 1997]	46
2.18	Response Curve of Sensor (SWNTs Functionalized with Pd) at Room Temperature [Sayago et al., 2005]	47
2.19	Plots of Resistance vs. Time for Ammonia [Villalpando-Paez et al., 2004]	48
2.20	Sensitivity vs. Ammonia Gas Concentration at the Operating Temperature of 330°C [Yun et al., 1997]	50
3.1	Chemical Vapor Deposition Setup	53
3.2	Hydrogen Calibration Curve	55
3.3	Scanning Probe Microscope (SPM) Apparatus Providing Atomic Force Microscope (AFM) mode	58
3.4	Ultrasonic Bath Case	59
3.5	Environmental Scanning Electron Microscope (ESEM)	62
3.6	Transmission Electron Microscope (TEM) Apparatus	64
3.7	Dropping Solution on the Carbon Grid	65
3.8	Internal Circuit of AFM	66
3.9	Source Measurement Unit (SMU)	67
3.10	Circuit for the 4-wire Measurement	68
3.11	Square Pellet (left) and Carbon Nanotubes Films on Glass Substrate (right)	69
3.12	Impedance Analyzer	70
3.13	Round Pellet with Silver Paint	71
3.14	Tool to Sandwich the Sample	72

3.15	Material Characterization Flow Chart	73
3.16	Setup for Gas Sensing	74
4.1	SEM Image of carbon nanotubes produced under temperature of 800°C	77
4.2	SEM Image of carbon nanotubes produced under temperature of 850°C	78
4.3	SEM Image of carbon nanotubes produced under temperature of 900°C	78
4.4	AFM Image of Carbon Nanotube	79
4.5	TEM Image of Carbon Nanotube	80
4.6	Structure of Carbon Nanotubes, (a), (b) and (c) Diameter and Wall Thickness for Three Different Samples	81
4.7	(a) Structure of Tube at Tube End and (b) Diameter and Wall Thickness at Tube End	82
4.8	I-V Curve Generated by Atomic Force Microscope (AFM)	83
4.9	I-V Curve for Electrode	84
4.10	Current-Voltage Curve for CNTs Pellet Samples	85
4.11	Current-Voltage Curve for CNTs Films Samples	86
4.12	Impedance of Carbon Nanotubes	89
4.13	Conductance of Material	90
4.14	Permittivity and Loss Factor of carbon Nanotubes	91
4.15	I-V Curve After the Gas Exposure for Pellet Sensor	93
4.16	I-V Curve After the Gas Exposure for Films Sensor	93
4.17	Variation of pellet sensor resistance upon exposure of CO ₂	95
4.18	Variation of films sensor resistance upon exposure of CO ₂	95
4.19	Configuration of Carbon Dioxide	96
4.20	Variation of pellet sensor resistance upon exposure of NH ₃	97
4.21	Variation of films sensor resistance upon exposure of NH ₃	98

4.22	Strong Bonding Ammonia to CNTs	99
4.23	Bonding of Valence Electron Forming Ammonia, NH_3	100
4.24	Variation of pellet sensor resistance upon exposure of C_2H_2	102
4.25	Variation of films sensor resistance upon exposure of C_2H_2	102
4.26	Electron Configuration of Acetylene	103
4.27	Reproducibility of Pellet Sensors (left) and films sensor (right) upon CO_2 Gas Exposure	105
4.28	Reproducibility of Pellet Sensors (left) and films sensor (right) Upon C_2H_2 Gas Exposure	105
4.29	Reproducibility of Pellet Sensors (left) and films sensor (right) upon NH_3 Gas Exposure	106

LIST OF ABBREVIATIONS

A	Ampere
AFM	Atomic Force Microscope
°C	Degree Celcius
C ₂ H ₂	Acetylene
C ₆ H ₆	Benzene
cm	centimeter
CNT	Carbon Nanotube
CO ₂	Carbon Dioxide
CVD	Chemical Vapor Deposition
FPD	Flat Panel Display
FCCVD	Floating Catalyst Chemical Vapor Deposition
Fe	Ferum
f_o	Resonant Frequency
f_z	Zero-Reactance Frequency
G	Conductance
HRTEM	High Resolution Transmission Electron Microscope
Hz	Hertz
IV	Current Voltage
K	Kelvin
MWNT	Multi Walled Carbon Nanotube
NH ₃	Ammonia
nm	Nanometer
Pd	Palladium

ppb	parts per billion
ppm	parts per million
R	Resistance
R_t	Reaction Time
R_T	Reaction Temperature
SEM	Scanning Electron Microscope
SiO_2	Silicon Dioxide
SMU	Source Measurement Unit
SPM	Scanning Probe Microscope
SWNT	Single Walled Carbon Nanotube
TEM	Transmission Electron Microscope
Tpa	Tera Pascal
V	Volt
μm	Micrometer
ϵ'	Permittivity
ϵ''	Loss Factor
Ω	Ohm
1-D	1 Dimensional
2-D	2 Dimensional

CHAPTER 1

INTRODUCTION

This chapter introduces the carbon nanotubes and its potential to act as a gas sensing element. Besides, it will also state the objectives of the study and scope within the research.

1.1 Nanotechnology

Nanotechnology relates to the creation of devices, structures and systems whose size ranges from 1 to 100 nm and exhibits novel physical, chemical and biological properties because of their nanoscale size. *Richard Feynman [Feynmann, 1959]* had emphasized in his lecture that nanotechnology is an interdisciplinary science, engineering and biology related dimensions on the order of few nanometers. The lecture is actually meant to stimulate new discoveries and capabilities at atomic and molecular scale. The exploration of nanotechnology is realized in 1980s as the scanning tunneling microscope emerged [*Meyyapan and Srivasta, 2000*].

Since the discovery in 1990 by Iijima, the very promising Carbon Nanotubes (CNT) have become a very potential nanotechnology materials in various applications such as interconnections, active switching element in electronic devices and gas sensing element in gas sensors due to their size in nanometer. The potential is stem from the features of carbon nanotubes structures, which are electronic, mechanical, optical and chemical



characteristics [McEuen *et al.*, 2001 and 2002, Avouris *et al.*, 2002, and Meyyappan and Srivasta, 2000].

1.2 Gas Sensing Element

As will be discussed in Chapter 2, carbon nanotubes are essentially all surface, thus they offer excellent sensitivity and rapid response towards surface changes. Furthermore, carbon nanotubes also possess a tendency to change electrical properties at room temperature in the presence of gases. Therefore, carbon nanotubes can be a good gas sensing element [Ong *et al.*, 2002 and Varghese *et al.*, 2001]. Electrical properties that are commonly used in detecting gases are resistance and impedance.

Gas sensing element to detect gases like Carbon Dioxide, Ammonia and Acetylene is needed to monitor the air quality. Ammonia sensor is important for monitoring ambient ammonia concentration since it is related to many environmental issues such as acidification, human health and climate change through particle formation. Carbon Dioxide sensors are widely used in food and medicine packages as a means of detecting spoilage [Ong, 2002]. Acetylene gas is widely used in chemical synthesis and also gas welding due to the high temperature of the flame produced from the combustion of Acetylene with oxygen. Therefore, the sensor is needed to detect Acetylene gas because Acetylene gas is odorless, colorless and can explode with extreme violence if the pressure of the gas exceeds 100kPa. Furthermore, inhaling Acetylene gas may cause dizziness, headache and nausea [<http://en.wikipedia.org/wiki/Acetylene>].

1.3 Problem Statement

Research on synthesis of carbon nanotubes has started in University Putra Malaysia (UPM) since 2003 by a research group from Chemical Engineering Department, Faculty of Engineering. However, all works were emphasized on investigating the mechanical and chemical properties of carbon nanotubes. There was no work dated to electrical characterization. In this research, electrical properties of carbon nanotubes will be investigated.

The electrical properties will be investigated towards the development of gas sensing element. As known, nowadays, the gas sensing element is needed in industry for environmental analysis, medical diagnostics and other various field applications. Other researchers have proposed gas sensing elements as reviewed in Section 2.5. Common gas sensors are in the form of thick films, porous pellets or thin films. Problems encountered with these sensors, which are lack of flexibility, poor response times and operating at elevated temperature. Therefore a new gas sensing element which is small in size, high sensitivity and can operate at room temperature is needed to solve the problems. In this research, the gas sensing element can give a quick response upon exposure to the gases and operate at the room temperature.