UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

PARAMETRIC STUDY OF ALIGNED CARBON NANOTUBE GROWTH USING ALCOHOL CATALYTIC CHEMICAL VAPOR DEPOSITION TECHNIQUE

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A thesis submitted
in fulfillment of the requirements for the degree of Master of Science
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DECLARATION

I declare that this thesis entitled "Parametric study of aligned carbon nanotube using alcohol catalytic chemical vapor deposition technique" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering.

Signature :……………..

Supervisor Name :……………………….....................................

Date :……………………..

DEDICATION

To my beloved family, lecturers and friends.

ABSTRACT

Carbon nanotubes (CNTs) are nanoscale materials with diameters of few nanometer and length up to several tens of microns. They have been widely used in various industrial applications such as energy storage devices, solar cell application and reinforcement for polymer composites. CNTs are commonly grown using catalytic chemical vapor deposition (CVD) technique. However, until now only few attempts have been made to study CNTs growth with detailed parameters on the growth of CNT alignment using alcohol as carbon feedstock. Thus, the main objective of this research is to further the study on the growth of aligned CNTs (A-CNTs) employing the said technique. A practical and high performance alcohol catalytic CVD (AC-CVD) system has been modified aimed at increasing the quality of gas flow which allows a greater amount of A-CNTs to be produced. The higher quality of gas flow could be produced through a unique shower ring gas supply located above the sample holder that could enhance the growth rate of A-CNTs. The radio frequency magnetron sputtering deposition technique was performed to prepare a substrate-supported catalyst. This consisting of silicon wafer substrate with 300 nm thick silicon oxide layer sputtered with aluminum as catalyst support and cobalt as catalyst with thickness of around 25 nm and below 10nm, respectively, were used to grow A-CNTs. Ethanol (C_2H_5OH) and argon (Ar) gas were used as CNT precursor and carrier gas, respectively. The AC-CVD processing temperature and time were varied at 700, 725, 750, 775, 800 °C and 3, 5, 7, 10, 15, 30 minutes, respectively, while other parameters were fixed. These parameters were chosen because 700 to 800 °C is the temperature range for CNT growth. Meanwhile, narrow initial time for AC-CVD processing time is due to the highly reactive growth of CNT at time under 10 minutes. The AC-CVD technique successfully produced CNTs with good alignment, high yield, and large area growth with improved controlling of the CNTs characteristics and morphologies. The CNT characterizations study were carried out using field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), as well as Raman spectroscopy. The best AC-CVD processing temperature and time were found to be at 725 °C and 10 minutes. The as-grown CNTs over various AC-CVD processing temperature and time showed high degree of graphitization, purity and density. The CNTs grown over cobalt catalyst on the silicon wafer substrate are according to the tip-growth mechanism.

ABSTRAK

Nanotiub karbon (CNT) adalah bahan dalam skala nano dengan diameter beberapa nanometer dengan panjang sehingga beberapa puluh mikron. Bahan ini digunakan dalam pelbagai aplikasi industri seperti peranti penyimpanan tenaga, aplikasi sel solar dan bahan pengukuh untuk komposit polimer. CNT biasanya dihasilkan menggunakan teknik pemendapan wap kimia pemangkin (CVD). Walau bagaimanapun, sehingga kini hanya beberapa percubaan telah dibuat untuk mengkaji penghasilan CNT dengan parameter terperinci terhadap penjajaran CNT menggunakan alkohol sebagai bahan mentah karbon. Dengan itu, objektif utama kajian ini adalah untuk membuat kajian lanjut pertumbuhan CNTs sejajar (A-CNT) menggunakan teknik ini. Sistem CVD pemangkin alkohol yang praktikal dan berkeupayaan tinggi telah diubahsuai dengan matlamat meningkatkan kualiti aliran gas yang seterusnya menghasilkan kuantiti A-CNTs yang lebih banyak. Aliran gas yang berkualiti tinggi boleh terbentuk melalui gegelang pancuran gas unik terletak diatas pemegang sampel yang boleh meningkatkan kadar pertumbuhan A-CNT. Teknik pemendapan pemercitan magnetron radio kekerapan dijalankan bagi penyediaan mangkin berpenyokong. Mangkin berpenyokong yang digunakan bagi menghasilkan A-CNTs adalah aluminium sebagai pemangkin sokongan dan kobalt sebgai pemangkin yang ditelapkan dengan ketebalan setikar 25 nm dan dibawah 10 nm di atas penyokong silicon wafer dengan lapisan silicon oksida berketebalan 300 nm. Etanol (C_2H_5OH) dan argon (Ar) diguna sebagai gas pemula dan gas pembawa. Suhu dan masa pemprosesan AC-CVD dipelbagaikan pada 700, 725, 750, 775, 800 °C dan 3, 5, 7, 10, 15, 30 minit, sementara parameter lain ditetapkan. Parameter ini dipilih kerana suhu 700 hingga 800 ° C adalah suhu pertumbuhan CNT. Sementara itu, perbezaan yang kecil parameter awalan untuk masa pemprosesan AC-CVD adalah disebabkan oleh pertumbuhan yang sangat reaktif CNT pada masa di bawah 10 minit. Teknik AC-CVD berjaya menghasilkan CNT dengan penjajaran yang baik, hasil yang tinggi, dan kawasan pertumbuhan yang luas dengan kawalan yang bertambah baik ciri-ciri dan morfologi CNT. Kajian pencirian CNT telah dilakukan dengan menggunakan teknik mikroskopi imbasan elektron pemancaran medan (FESEM), mikroskopi transmisi elektron (TEM) serta spektroskopi Raman. Suhu dan masa pemprosesan AC-CVD yang baik telah dikenalpasti pada 725 °C dan 10 minit. CNT tersedia atas pelbagai suhu dan masa pemprosesan AC-CVD menunjukkan darjah grafitasi, ketulenan dan kepadatan yang tinggi. Pertumbuhan CNT keatas mangkin kobalt berpenyokong wafer silicon didapati selaras dengan mekanisma pertumbuhan hujung.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURES

CNT	-	Carbon nanotube
HR-TEM	-	High-resolution transmission electron microscopy
CVD	-	Chemical vapor deposition
AC-CVD	-	Alcohol catalytic chemical vapor deposition
nm	-	Nanometer
A-CNT	-	Aligned carbon nanotube
FE-SEM	-	Field emission scanning electron microscopy
TEM	-	Transmission electron microscopy
C_{60}	-	Fullerenes
0-D	-	Zero-dimensional
1-D	-	One-dimensional
2-D	-	Two-dimensional
3-D	-	Three-dimensional
m	-	Meter
MWCNT	-	Multi-walled carbon nanotube
SWCNT	-	Single-walled carbon nanotube
STM	-	Scanning tunnelling microscopy
A-MWCNT	-	Aligned multi-walled carbon nanotube
Ω	-	Ohm
ω	-	Omega
W	-	Watt
mK	-	Millikelvin
°C	-	Degree celcius
cm^2	-	Centimeter squared
TPa	-	Terapascal
GPa	-	Gigapascal

V	-	Volt
µm	-	Micrometer
Co	-	Cobalt
Fe	-	Iron
Si	-	Silicon
Ti	-	Titanium
Al_2O_3	-	Aluminum oxide
AAO	-	Anodic aluminum oxidation
Al	-	Aluminum
cm/min	-	Centimeter per minute
kPa	-	Kilopascal
EB-PVD	-	Electron beam physical vapor deposition
Pa	-	Pascal
VLS	-	Vapor-liquid-solid
A-SWCNT	-	Aligned single-walled carbon nanotube
VA-SWCNT	-	Vertically aligned single-walled carbon nanotube
AFM	-	Atomic force microscopy
VA-CNT	-	Vertically aligned carbon nanotube
N/cm^2	-	Newton per square centimeter
EM	-	Electron microscopy
SEM	-	Scanning electron microscopy
keV	-	Kiloelectron volt
CA	-	Condenser aperture
CL	-	Condenser lens
FP	-	Focal point
OL	-	Objective lens
eV	-	Electron volt
kV	-	Kilovolt
G peak	-	Graphite peak
D peak	-	Defect
RBM	-	Radical breathing mode
C_2H_2	-	Acetylene
NH_3	-	Ammonia

RF	-	Radio frequency
MiNT-SRC	-	Microelectronis and nanotechnology - Shamsuddin research center
cm	-	Centimeter
mm	-	Millimeter
Ar	-	Argon
MFC	-	Mass flow controller
kW	-	Kilowatt
PID	-	Proportional-integral-derivative
N	-	Nitrogen
sccm	-	Standard cubic centimeters per minute
SiO_2	-	Silicon oxide
Al-O	-	Thermally oxidize aluminum
EDX	-	Energy-dispersive x-ray spectroscopy
I_G/I_D	-	Relative intensity of D-band and G-band
d	-	Diameter
Δn	-	Rayleigh line

LIST OF PUBLICATIONS

Bistamam, M.S.A., Azam, M.A., Manaf, N.S.A., Goh, P.S., Rashid, M.W.A., Fauzi, A.F., 2014. An overview of selected catalytic chemical vapor deposition parameter for aligned carbon nanotube growth. *Nanoscience and Nanotechnology - Asia*, 4, pp. 2-30.

Bistamam, M.S.A., Azam, M.A., 2014. Tip-growth of aligned carbon nanotubes on cobalt catalyst supported by alumina using alcohol catalytic chemical vapor deposition. *Results in Physics*, 4, pp. 105-106.

Manaf, N.S.A., Bistamam, M.S.A., Azam, M.A., 2013. Development of high performance electrochemical capacitor: A systematic review of electrode fabrication technique based on different carbon materials. *ECS Journal of Solid State Science and Technology*, 2, pp. M3101-M3119.

Azam, M.A., Manaf, N.S.A., Talib, E., Bistamam, M.S.A., 2013. Aligned carbon nanotube from catalytic chemical vapor deposition technique for energy storage device: A review. *Ionics*, 19, pp. 1455-1476.

CHAPTER 1

INTRODUCTION

1.1 Background

Nanoscience is an exciting field of study that brought us into nanomaterials exploration. The prefix nano means one-billionth of something like a meter or a second, in comparison 1 nm is 10000 times smaller than the average diameter of a human hair. In principle, nanomaterials are described as materials with at least one external dimension in the nanometer length scale of 1-100 nm. The exploitation of novel phenomena and properties of nanomaterials can enable ground-breaking, as opposed to conventional, advances in science and technology that offer the tools to understand and control how materials are made at the atomic and molecular level. The understandability and controllability at this level could open new paths to create new materials that subsequently leads to developing new devices are unlimited (Rao et al., 2005).

Generally, utmost significant impact in this field was triggered by a breakthrough in nanomaterial synthesis. Therefore, tremendous effort in material syntheses are being enthusiastically conducted by researchers and scientists globally to achieve the rational approaches that regarded as the vital point to successfully synthesizes new materials. Nonetheless it is still far from done, these nanomaterials essentially need to be assembled hierarchically and developed into complex and functional architectural elements for devices and applications. The explorations in hierarchical assembly of nanomaterials enable the development of architectural elements that have innovative and rational structures and functions, in addition to perceive their fundamental properties (Jariwala et al., 2013). Unfortunately, in numerous occasions the unique fundamental properties are yet to be known, thus the possible applications are also unknown.

In recent decades, carbon nanomaterials have been the hot topic in nanoscience and nanotechnology field due to their extraordinary electrical, thermal, mechanical and chemical properties and have the supreme potential to be utilized as energy storage and conversion, composite materials, field emission devices, drug delivery, sensors and nanoscale electronic components (O'Connel, 2006). Carbon nanomaterials are nanostructure composed of carbon atoms and have more than one form, from 0-D to 3-D. One of the most well-known carbon nanomaterials is carbon nanotube (CNT) and was first reported in literature by Baker et al. (1972, 1973) but termed as filamentous carbon. These reports did not simulate the interest of the research on CNT but only the mechanism for filament growth. The real breakthrough came almost 20 years later with the experimental observation of CNTs in 1991 by Iijima using high-resolution transmission electron microscopy (HR-TEM) (Iijima, 1991). Since that, the studies on CNTs grew rapidly due to the unique structures and properties of CNTs.

The rapid advancement in the field of nanoscience and nanotechnology with the need for commercialization of CNTs product at large-scale has led the necessity to develop efficient growth techniques. Various techniques have been developed to growth CNTs including arc discharge, laser ablation, and chemical vapor deposition (CVD). Among these techniques, CVD using alcohol as carbon feedstock known as alcohol catalytic chemical vapor deposition (AC-CVD) is among the promising technique to grow CNTs (Murakami et al., 2003a) which is well known for its economical merit, wide selectivity of substrates, better catalytic reaction, and ability to grow high purity CNTs. CNTs especially aligned CNTs (A-CNTs) have numerous potential applications in nanoelectronics, field emission devices, and biological probes, among others. Thus in order to accomplish CNTs full potential, better understanding on the CNT growth become essential for those who working in this area.

1.2 Problem statement

The focal hindrance in CNTs is the inability to control the growth of the nanotubes and these nanotubes constantly contain a vast amount of defects along the length of the tubules. In addition, serious weakness for synthesizing carbon nanomaterials particularly CNTs is the grown CNTs yield a wide range of diameters and structures. This possibly not the issue for some applications, however it could be a drawback in areas where specific tube diameters or structures with uniform properties are needed, such as in nanoelectronics. CVD parameter including processing temperature, time, pressure, and gas composition significantly influences the CNT growth. Although there are abundant reports on CVD parameter influence on CNT growth (Bistamam et al., 2014a), the replication on the growth result is challenging even using the same CVD setup. Apropos to the shortcoming, a slight different in CVD setup is likely to result a very different outcome.

AC-CVD is one of the techniques to grow CNTs and this technique will lead to the formation of high quality and purity of CNTs. However, this technique is still not quite well studied. Appropriate growth's parametric study is critical to support any application-basis research. In specific, research on typical A-CNT growth using AC-CVD was not well discussed in recent years; best growth condition shall depend on requested applications.

Indeed, the lack of understanding in CNT growth especially CNTs with alignment on different CVD processing temperature and time by AC-CVD is the primary motivation in present work. The parameter range used in this experiment varied from the wide range of previously used for A-CNT growth by other researchers using different equipment setup (Bistamam et al., 2014a), C-CVD processing temperature of 700 to 800 °C and C-CVD processing time of 3 to 30 minutes.. These ranges are believed to be the range for A-CNT growth. Herein, a newly setup AC-CVD system is designed for A-CNT growth by verifying aforementioned parameter to grow high yield and quality A-CNTs. The results might lead to an explanation and better understanding of the role of the CVD processing temperature and time in A-CNT growth at different temperature and time setup.

1.3 Research objectives

The main aim of this work was to grow aligned carbon nanotubes using our newly setup alcohol catalytic chemical vapor deposition system and study the alcohol catalytic chemical vapor deposition processing parameters influence on the aligned carbon nanotube growth result. The specific objectives are:

a) To analyze the effect of AC-CVD processing temperature and time on the morphology of A-CNTs.
b) To characterize the morphologies of A-CNTs produced using AC-CVD using FE-SEM and TEM.
c) To characterize the structural changes and graphitization of A-CNTs produced using AC-CVD using Raman spectroscopy.

1.4 Scope of study

In order to fulfill the research objectives, the following scope were outlined: The scope can be divided into six major tasks; a) CVD system modification, b) the deposition of catalyst thin film, c) characterization of catalyst thin film, d) growth of A-CNTs e) characterization of as grown A-CNTs), and f) suggest A-CNT growth mechanism.

a) Modification of AC-CVD system.
b) Depositing aluminum (Al) and cobalt (Co) thin film with thickness of 20~30 nm and 1~10 nm, respectively. Al will act as catalyst support and Co as catalyst for CNT growth.
c) Characterizing the Co and Al using surface profiler and FE-SEM.
d) Growing the A-CNTs by varying the AC-CVD processing temperature (700~800 °C) and time (1~30 minutes).
e) Studying the morphology of the surface and comparing the surface morphology of the samples with various growth conditions, carbon nanostructures are characterized by FE-SEM and TEM. Raman spectroscopy will be used to observe the change of phases, purities of the samples and effect of the AC-CVD processing parameters on the CNTs formation.
f) Suggest the growth mechanism of A-CNT to further understand how the formation of CNT. The suggestion will be based on the characterization done by FE-SEM, TEM, and Raman spectroscopy.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon materials

Carbon is among one of the most important elements and a key element for a variety of matter. It exists in several polymorphic forms. The most well-known carbon is graphite commonly found in the cores of pencils and diamond commonly found on engagement rings. These are two bulk forms of carbon illustrated in Figure 2.1. In diamond, each atom shares a bond with every neighboring atom, forming a tetrahedral structure. On the other hand, graphite has a layered, planar structure. In addition to these two forms, a new allotrope of carbon, called a fullerene, was discovered by Kroto et al., (1985), a breakthrough for which they were awarded the Nobel Prize in chemistry in 1996. The most well-known of these fullerenes is the "buckyball", or C_{60}. Due to its spherical symmetry and small size (consisting of 60 atoms), it is essentially a zero-dimensional (0-D) material, also known as a quantum dot.

The discovery of fullerenes make the members of the carbon included the 3-D forms of diamond and graphite, 2-D graphene, and 0-D fullerenes. So what about a 1-D carbon allotrope? One can imagine forming a 1-D carbon allotrope by either elongating a buckyball, or by rolling up a 2-D graphene sheet into a narrow, tubular structure. This is exactly the structure discovered in 1993 (Iijima and Ichihashi, 1993; Bethune et al., 1993), and is known as a single-walled carbon nanotube (SWCNT). In fact, both single- and multi-walled forms (Iijima, 1991; Oberlin