UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OD A PULSED LASER ABLATION TECHNIQUE FOR THE FORMATION OF CARBON NANOTUBES

BEH HOE GUAN.

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DEVELOPMENT OF A PULSED LASER ABLATION TECHNIQUE FOR THE FORMATION OF CARBON NANOTUBES

By

BEH HOE GUAN

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

May 2006

Dedicated to:

My parents, sister and to all those who has supported me throughout my studies.

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

DEVELOPMENT OF A PULSED LASER ABLATION TECHNIQUE FOR THE FORMATION OF CARBON NANOTUBES

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BEH HOE GUAN

May 2006

Chairman : Noorhana Bt Yahya, PhD

Faculty : Science

The objective of this work was to develop a pulsed laser ablation technique for the formation of carbon nanotubes (CNTs). This study was divided into three parts. The first part involved the development of pulsed laser ablation (PLA) system. The second part dealt with the growth of CNTs by using the pulsed laser ablation technique, and finally the last part dealt with the analysis of microstructure and surface morphology of the deposited sample collected and the influence of the laser ablation on the surface morphology of the sample target.

A vacuum chamber was designed for the formation of CNTs. The stainless steel chamber used in this system has a cylindrical shape, with diameter of about 15cm and 45cm length. CNTs were formed by laser ablation using a graphite pellet, graphite-Ni, graphite-Co and graphite-Ni-Co, each with 10 weight percentage catalysts. The Nd:YAG laser with 532nm wavelength, 10.24 W laser power was used to ablate the target to form the CNTs. Argon (Ar) gas was kept flowing into the chamber, keeping the pressure inside chamber at 4 Torr.

Web-liked CNTs were found in the deposited sample collected after 30 minutes laser ablation by using the graphite pellet and the graphite filled with mono-catalyst and bi-catalyst. The XRD pattern for the deposited sample shows the CNTs peak located at about 26.5°. The SEM micrograph show that the diameter size of the CNTs formed by the Co, Ni, NiCo catalysts and without catalyst follow the order C>CCo>CNi>CNiCo. The range of the diameters of the CNTs was found to be about 35-150nm. The sphere-liked carbon structures were found deposited in the substrate after laser ablation without the Ar gas flowing into the chamber during the ablation process. TEM micrograph confirmed the formation of CNTs. It was found that by using a bi-metal catalyst (Ni-Co), a bamboo-like structure of CNTs was formed.

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

PEMBANGUNAN TEKNIK DENYUTAN ABLASI LASER UNTUK PENGHASILAN NANOTIUB KARBON

Oleh

BEH HOE GUAN

Mei 2006

Pengerusi : Noorhana Bt Yahya, PhD

Fakulti : Sains

Objektif kerja ini adalah untuk membangunkan teknik denyutan ablasi laser untuk penghasilan nanotiub karbon. Kajian ini dibahagikan kepada 3 bahagian. Bahagian pertama, melibatkan pembangunan teknik denyutan ablasi laser. Bahagian kedua, menggunakan teknik denyutan ablasi laser untuk menghasilkan nanotiub karbon, dan bahagian yang terakhir adalah analisis mikro struktur dan morfologi permukaan sampel yang dihasilkan dan pengaruh ablasi laser pada morfologi permukaan sampel sasaran.

Kebuk telah dibangunkan untuk menghasilkan nanotiub karbon. Kebuk besi nir-karat yang digunakan dalam denyutan ablasi laser mempunyai bentuk silinder, dan diameter adalah 15sm dan panjang adalah 45sm. Nanotiub karbon telah dihasilkan oleh ablasi laser dengan menggunakan pelet grafit, grafit-Ni, grafit-Co dan grafit-Ni-Co, dengan peratus berat untuk setiap sampel adalah 10. Laser Nd:YAG dengan panjang gelombang 532nm dan kuasa 10.24 W telah digunakan untuk ablasi sasaran

sampel untuk menghasilkan nanotiub karbon. Gas Argon (Ar) telah dialirkan ke dalam kebuk dan tekanan dalam kebuk ditetapkan pada 4 Torr.

Nanotiub karbon berbentuk jaring telah ditemui dalam sampel yang dihasilkan selepas 30 min ablasi laser dengan menggunakan pelet grafit dan pelet grafit yang dicampurkan dengan mono-mangkin dan bi-mangkin. Keputusan XRD menunjukkan nanotiub karbon puncak pada 26.5^{o}. SEM mikrograf menunjukkan diameter nanotiub karbon yang dihasilkan dengan menggunakan mangkin Co, Ni, NiCo dan tidak menpunyai mangkin mengikuti susunan C>CCo>CNi>CNiCo. Julat saiz diameter nanotiub karbon yang ditemui adalah 35-150nm. Bentuk sfera struktur karbon didapati kumpul di atas substrat selepas ablasi laser dengan tiada gas Ar dialirkan ke dalam kebuk pada masa proses ablasi. TEM mikrograf telah menentukan penghasilan nanotiub karbon. Nanotiub karbon struktur berbentuk buluh telah ditemui dengan menggunakan mangkin NiCo.

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I certify that an Examination Committee has met on 18th May 2006 to conduct the final examination of Beh Hoe Guan on his Master of Science thesis entitled "Development of a Pulsed Laser Ablation Technique for the Formation of Carbon Nanotubes" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis 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 are as follows:

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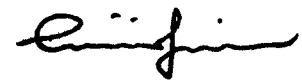

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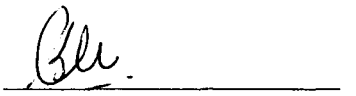
DECLARATION

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.



BEH HOE GUAN

Date: 13/06/06

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LIST OF ABBREVIATIONS

YAG	Yttrium Aluminium Garnet
PLA	Pulsed Laser Ablation
CNTs	Carbon Nanotubes
SWNTs	Single Wall Carbon Nanotubes
MWNTs	Multi Wall Carbon Nanotubes
XRD	X-Ray diffractometer
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
EDX	Energy Dispersive X-ray
at%	Atomic percentages
$\Delta L/L_o$	Thermal expansion
E	Young's modulus
T_m	Melting point
LIPSS	Laser-Induced Periodic Surface Structures
CVD	Chemical Vapor Deposition
d_{hkl}	Lattice spacing
hkl	Miller indices
r.p.m	Round per minute
Ar	Argon

CHAPTER 1

INTRODUCTION

1.1 Introduction

In recent years nanotechnology has become one of the most important and exciting forefront field in physics, biology, chemistry and engineering. Nanotechnology is deals with structures which are smaller than 100nm impart to nanostructures built from them a new chemistry and physics, leading to new behavior which depends on the size. The conductivity, mechanical and electrical properties have all been observed to change when the particles become smaller than a critical size. The reduction of size into the nanometer size often results in characteristic properties of substances and materials which can be exploited for new applications and which do not appear in macroscopic pieces of the same materials. These include significantly higher hardness, breaking strength and toughness at low temperatures, the emergence of additional electronic states, and high chemical selectivity of surface sites and significantly increased surface energy. Because of this technology has enormous potential to contribute to significant advances over the wide and diverse range of technologies areas, nanotechnology not will only influence technological development in the near future, but will also have economic and society impact.

Promising application of carbon nanotubes (CNTs) represent an interesting new era of nanotechnology. Various nanotubes are promising because of their unusual mechanical, electronic properties and stability. CNTs were discovered accidentally by Sumio Iijima in 1991, while studying the surfaces of graphite electrodes used in

an electric arc discharge (Iijima., 1991). A year later, Thomas Ebbesen and P.M Ajayan at NEC found a way to produce these nanotubes in high yields and make them available for studies by different technique. In 1996, Smalley and Robert Curt were awarded a Nobel Prize in Chemistry for this field of work (Yahya et al., 2004).

CNTs are made of sheets of carbon atoms with a cylindrical shape, and generally consist of co-axially arranged 2 to 20 cylinders with maximum length up to a fraction of micrometer. Each cylinder of the tubules is made by rolling a honeycomb sheet of carbon atom hexagonal rings. Furthermore, in many cases the hexagons are arranged on a cylinder with a helical pattern along the tube axis. CNTs of a single-atom wall thickness have been discovered, with much smaller diameters, of the order of one molecule. Such small CNTs are expected to show some unique properties not seen in conventional materials. Other unique properties of the CNTs include surface dominant structures where all atoms are facing to the surface, superb mechanical strength, flexibility, chemically and thermally stable materials.

Since the discovery of CNTs many techniques have been created to produce the high quality of CNTs. The earliest approach to produce nanotube was an arc process as pioneered by Iijima (Iijima et al., 1991). Three of the techniques have become a common technique to grow nanotubes; there are Chemical Vapor Depositions (CVD) (Dai et al., 1996; Su et al., 2000; Delzeit et al., 2001), Arc discharge (Ebbesen et al., 1993; Seraphin et al., 1993; Journet et al., 1997) and Pulsed Laser Ablation (PLA) (Zhigilei et al., 1999; Sen et al., 2000; Wal et al., 2003). The effects of various processing conditions on the growth yield of CNTs for these techniques were extensively studied by many researchers (Ajayan et al., 1993; Li et al., 2001; Kukovitsky et al., 2002).

A successful production of SWNTs (Single Wall Carbon Nanotubes) by using technique laser ablation has been reported, the yield of SWNTs out of the carbon consumed more than 70% (Yudasaka et al., 1997). In addition to the growth of thin films by pulsed laser deposition, laser vaporization is an established nanomaterial synthesis tool. Laser ablation method is the very useful and powerful technique for producing CNTs. In this technique, a Co/Ni graphite composite pellet was used as a target, where the graphite pellet with some metal catalysts absorbs the laser beam, heat up and transforms into molten carbon (C). When the ambient pressure is high, the NiCo particles in the target gain heat from the laser and form a solution with the molten C. Droplets of the molten C containing Ni and Co were expelled from the target and deposited to the substrate.

1.1.1 Potential application of carbon nanotubes

Since the discovery of CNTs, many studies on the formation, structure and properties of CNTs have been made (Yudasaka et al., 1997). Nanotubes have remarkable mechanical, electrical and thermal properties with strong, light and high toughness characteristics. The most important application of nanotubes based on their mechanical properties will be as reinforcements in composite materials.

Since nanotubes have relatively straight and narrow channels in their cores, it was speculated from the beginning that it might be possible to fill these cavities with foreign materials to fabricate one-dimensional nanowires. A large body of work now exists to concerning the filling of nanotubes with metallic and ceramic materials. Thus, nanotubes have been used as templates to create nanowires of various compositions and structures (Ebbesen, 1997).

When a small electric field is applied parallel to the axis of a nanotube, electrons are emitted at a very high rate from the ends of the tube. This is called field emission. This effect can easily be observed by applying a small voltage between two parallel metal electrodes, and spreading a composite paste of nanotubes on one electrode. A sufficient number of tubes will be perpendicular to the electrode so that electron emission can be observed. One application of this effect is the development of flat panel displays (Poole, 2003).

CNTs have applications in battery technology. Lithium, which is a charge carrier in some batteries, can be stored inside CNTs. It is estimated that one lithium atom can be stored for every six carbons of the tube. Storing hydrogen in CNTs is another possible application, one that is related to the development of fuel cell as sources of electrical energy for future automobiles. A fuel cell consists of two electrodes separated by a special electrolyte that allows hydrogen ions, but not electrons, to pass through it. Hydrogen is sent to the anode, where it is ionized. The freed electrons travel through an external circuit wire to the cathode. The hydrogen ions diffuse through the electrolyte to the cathode, where electrons, hydrogen, and oxygen combine to form water. The system needs a source of hydrogen. One possibility is to store the hydrogen inside CNTs (Poole, 2003)

The high electrical conductivity of CNTs means that they will be poor transmitters of electromagnetic energy. A plastic composite of CNTs could provide lightweight shielding materials for electromagnetic radiation (Poole, 2003).