STRUCTURAL AND OPTICAL PROPERTIES OF CARBON NANOWALLS BY PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION METHOD

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to my parents,
Subari Bin Yarmo and Zaiton Binti Omar;
my husband and all my friends,
without whom none of my success would be possible

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ABSTRACT

Vertically aligned carbon nanowalls (CNWs) were synthesized by catalyst-free 150 MHz high frequency plasma enhanced chemical vapor deposition (PECVD) system, where methane and hydrogen gases were used as the reactive gases. Parametric studies were done to determine the optimum parameters required to obtain tuneable growth of CNWs with favourable properties at high quality film. The parameters included are the optimized temperature, rf power and methane flow-rate. The effects of the growth conditions on the optical properties of the samples were investigated by UV-Vis-NIR spectroscopy and photoluminescence (PL) spectroscopy, while the morphologies and structural properties were characterized by Micro-Raman scattering, Fourier transform infrared (FTIR) spectroscopy and field emission scanning electron microscopy. Shape, density and quality of CNWs were extensively studied and found to be significantly affected by the synthesis parameters. Based on the investigation of the morphologies of catalyst-free CNWs deposited on silicon substrate, it was observed that the optimized parameters have specific range of values. The synthesis temperature, rf power and methane flow-rate are in range of 750-800^{o}C, 10-40 watt and 14-18 sccm, respectively. The morphologies of CNWs produced in different growth conditions looked quite similar but significant thinning of the walls was observed. Wall thickness and height of CNWs were strongly dependent on growth conditions while the lengths were not greatly affected. In Raman spectrum of CNWs, there were four peaks which consist of a low intensity D band, a sharp and strong G band, and low intensity 2D band and D + G band. The intensity ratio of the D band to G band was about 0.15 which indicates a lower number of defects in the CNW structures. FTIR results showed that the absorption band can be associated to the structural vibration of CNWs. From UV-Vis-NIR measurement, the minimum reflectance was found at 0.011 % which indicates that this material is a good candidate for use in a blackbody-like coating. The PL result of the CNW films produced one peak which signifies a narrow opening band gap indicating the presence of an epitaxial bilayer graphene. The energy gap of the CNWs was 1.92 eV which can be regarded as a semiconductor-like characteristic. Tuneable CNWs synthesized using 150 MHz PECVD method can be considered as a good candidate for materials used in optical and optoelectronic devices.

ABSTRAK

Nanotembok karbon berjajaran tegak (CNWs) telah disintesis menggunakan sistem pemendapan wap kimia secara peningkatan plasma berfrekuensi tinggi (PECVD) 150 MHz bebas-pemangkin, di mana gas metana dan hidrogen telah digunakan sebagai gas reaktif. Kajian berparameter telah dilakukan untuk menentukan parameter optimum bagi mendapatkan pertumbuhan terkawal CNWs dengan sifat-sifat baik untuk menghasilkan filem yang berkualiti tinggi. Parameter termasuklah suhu, kuasa rf dan kadar aliran metana. Kesan daripada keadaan pertumbuhan terhadap sifat optik sampel telah disiasat menggunakan spektroskopi UV-Vis-NIR dan spektroskopi luminesens foto (PL), manakala sifat morfologi dan struktur telah dicirikan menggunakan spektroskopi serakan mikro-Raman, spektroskopi transformasi Fourier inframerah (FTIR) dan mikroskopik pengimbasan elektron bermedan pancaran. Bentuk, ketumpatan dan kualiti CNWs telah dikaji secara terperinci dan didapati dipengaruhi oleh parameter sintesis. Berdasarkan kajian morfologi CNWs bebas-pemangkin yang dimendapkan pada substrat silikon, diperhatikan bahawa parameter optimum mempunyai nilai pada julat tertentu. Suhu, kuasa rf dan kadar aliran metana sintesis masing-masing berada dalam julat 750-800°C, 10-40 watt dan 14-18 sccm. Sifat morfologi CNWs yang dihasilkan pada keadaan pertumbuhan berbeza kelihatan agak sama tetapi penipisan dinding yang ketara diperhatikan. Ketebalan dinding dan ketinggian CNWs adalah sangat bergantung kepada keadaan pertumbuhan manakala panjangnya tidak terjejas dengan ketara. Dari serakan Raman CNWs, terdapat empat puncak yang terdiri daripada jalur D berkeamatan rendah, jalur G yang tajam dan kuat serta jalur 2D dan jalur D+G berkeamatan rendah. Nilai nisbah keamatan jalur D kepada jalur G ialah 0.15 yang menunjukkan kehadiran kecacatan rendah dalam struktur CNWs. Keputusan FTIR menunjukkan jalur penyerapan boleh dikaitkan kepada getaran struktur CNWs. Daripada pengukuran UV-Vis-NIR, pantulan minimum yang didapati ialah 0.011% yang menunjukkan bahan ini adalah calon sesuai untuk salutan mirip jasad hitam. Hasil keputusan PL di filem CNWs menghasilkan satu puncak yang menandakan pembukaan jurang tenaga sempit menunjukkan kewujudan grafen dwilapisan epitaksi. Jurang tenaga CNWs ialah 1.92 eV yang boleh dianggap sebagai ciri bahan mirip semikonduktor. CNWs yang disintesis secara terkawal dengan kaedah 150 MHz PECVD boleh dianggap sebagai calon yang sesuai dalam penggunaan bahan dalam peranti optik dan optoelektronik.

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LIST OF SYMBOLS

sccm - Standard cubic centimeter (unit of flow rate)

mTorr - Mili-Torr (unit of pressure)

V - Volt (unit of electrical energy)

kV - Kilo-volt

V/μm - Volt per micro-meter

L/s - Liter per seconds (unit of flow rate/pumping speed)

cm^{-1} - One per centi-meter (unit of wavenumber)

°C - Degree celcius (unit of temperature)

W - Watt (unit of power)

Ω - Ohm (unit of electrical resistance)

% - Percentage

MHz - Mega-Hertz (unit of frequency)

Ar - Argon gas

Al_2O_3 - Aluminium Oxide or alumina

C_2 - Carbon radicals

CH_3 - Hydrocarbon radicals of CH_3

CH_4 - Methane gas

CH_x - Hydrocarbon radicals of CH (with x =1,2,3)

C_2H_2 - Acetylene gas

C_2F_6 - Hexafluoroethane gas

C_4F_6 - Hexafluoro-2-butyne gas

CF_4 - Tetrafluoromethane gas

CFH_3 - Fluoromethane free radicals

Cu-Kα - Copper-K alpha X-ray source

ED - Electrode distance

Gt - Growth time

H - Hydrogen atom or radicals

H_2 - Hydrogen gas

N_2 - Nitrogen gas

NH_3 - Ammonia

Ni - Nickel catalyst

NiFe - Nickel-Ferrite catalyst

SiO_2 - Silicon dioxide

SiO_x - Silicon oxide (x=integer)

SiN_x - Silicon nitride (x=integer)

sp_2 - sp_2 molecular bonding or orbitals

sp_3 - sp_3 molecular bonding or orbitals

$\lambda\alpha$ - Wavelength of X-ray beam

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Carbon nanomaterials history starts in a recent two decades where it is still in development. The first carbon filaments of nanometer dimensions were prepared in 1970s by Morinobu Endo where he grew carbon fibres about 7 nm in diameter using a vapour growth technique but these filaments were not recognized as nanotubes and not studied systematically (Yang, 2004). At 1991, Sumio Iijima found carbon nanotubes (CNT) when using high-resolution transmission electron microscopy and the study nanostructure carbon research start to take off (Sumio, 1991). Researchers at the Institute of Chemical Physics in Moscow discovered CNT and nanotube bundles at about the same time, but these generally had a much smaller length-to-diameter ratio (Yang, 2004). There are two fundamentally opposite approaches to nanotechnology, called “top-down” and “bottom-up”. Nanomaterials constitute a field in which nanotechnology has had much success, thanks to “bottom-up” approach, in which the organic and inorganic structures are built atom-by-atom, or molecule-by-molecule, such as fullerenes, carbon nanotubes, nanoparticles, nanowires, nanorods, nanobelts, nanofoams and nanowalls. Among all, carbon nanowalls (CNWs) have long been a subject of interest.

Carbon is a unique element due to its ability to form a variety of nanomaterial depends on their dimensionality, it can be divided into four categories: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D). The classification is introduced such as fullerenes (0D), carbon nanotubes (1D), graphene (2D) and diamond (3D). These carbon based nanomaterials have remarkable physical properties and have received specific attention for a variety of applications such as biomedical field (Himani, 2012).

CNWs are a graphite sheet nanostructure with edges that are composed of stacks of planar graphene sheets standing almost vertically on the substrate. In addition, the sheets form a self-supported network of wall structures with thickness in nanometers range and have high aspect ratio (Mineo *et.al.,* 2010). CNWs consist of graphene sheets and are expected to have high mobility for carriers and large sustainable current densities where CNWs are considered to be one of the most promising carbon materials used for nanoscale electronic devices. Furthermore, the morphology and structure of carbon nanowall film are depending on gases, pressure, process temperature, as well as the type of plasma used during the growth. The isolated nanosheets, vertically a standing nanowall with a maze-like structure, highly branched type, and a kind of porous film have been fabricated for various application (Yihong *et.al.*, 2014). For graphene applications, the isolated and aligned structure may be desirable for the electron emitters. In the case of the application for membrane filter, honeycomb structure with controlled spacing is required. Moreover, less aligned and dense carbon nanowall films with large surface area can be used for gas storage application (Mineo *et.al.*, 2010; Yihong *et.al.*, 2014).

The characteristics of CNW films are demonstrated as the optical properties in the visible range are close to a peRFect light absorber which is the black body. The black body is a simple physical model which is well known from the school optics course, and it remains highly demanded for a wide range of implementations and solutions for many technological issues. Apparently, a practical preparation of the black body-like materials will bring benefits to many fields such as sensing, radiometric and energy harvesting. This material can absorb light almost peRFectly in a very wide spectral range. Compared to a CNT forest with a thickness of hundreds of microns, the CNWs films are much thinner (only by several microns) and hence the specific light absorption characteristics (normalized by the film mass per substrate area) are essentially higher (Krivchenko *et.al.*, 2013). For structural analysis works on the principle of inelastically scattered light. When light is incident on a sample, it can be transmitted, absorbed and/or scattered. The scattered light interacts both elastically and inelastically with the sample. Inelastic scattering is nothing but the frequency of photons in monochromatic light is changed by interaction with the sample. The sample absorbs the photons of the laser light and re-emits it. In comparison to the original laser light frequency the reemitted frequency changes (shifted up or down) which is basically called the Raman Effect. This change or shift provides information about transitions in molecules i.e. vibrational or rotational ones. Raman scattering is an optical process involving the simultaneous emission or absorption of a phonon associated with the scattering of a photon (Jackson, 2011; Zhenhua, 2007).

In these recent years, many other experimental method have been made in order to fabricate of CNWs. Synthesis methods for CNWs are similar for those who used it for diamond films and carbon nanotubes. In general, a mixture of hydrocarbon and hydrogen or argon gases, typically CH_4 and H_2, is used as a source gas for the synthesis of CNWs (Zhenhua, 2007; Mineo *et.al.*, 2010). High-density plasmas which are microwave plasma and inductively coupled plasma suitable for decomposing H_2 molecules efficiently because a large amount of H atoms is required for the growth of CNWs, which is similar to diamond growth (Zhenhua, 2007). In addition, these CNWs and other related materials have been grown using various CVD methods such as microwave plasma (Wu *et.al.*, 2002; Chuang *et.al.*, 2007), radio frequency (RF) inductively coupled plasma (Wang JJ *et.al.*, 2004), RF capacitively coupled plasma assisted by H radical injection (Hiramatsu M. *et.al.*, 2004 , Hiramatsu M. *et.al.*, 2006), helicon-wave plasma (Sato G. *et.al.*, 2006), electron beam excited plasma (Mori T. *et.al.*, 2008), hot-filament CVD (Shimabukuro S. *et.al.*, 2008), and even by sputtering of a graphite target (Zhang H. *et.al.*, 2004). Pressures are ranging from a few mTorr to atmospheric pressure. Metal catalysts such as Fe and Co are required for the growth of carbon nanotubes, whereas

CNWs do not require such catalysts. Consequently, CNWs have been fabricated on several substrates, including Si, SiO_2, Al_2O_3, Ni, and stainless steel, at substrate temperatures of 500–700°C without the use of catalysts (Shiji K. *et.al.*, 2005).

From previous research, it shown that the VHF-PECVD method is more suitable for the growth of a high quality CNWs. It is suggested the VHF-PECVD method possess electrical field and ionic species contribute to the growth of CNWs. The advantage of VHF-PECVD method shows that it is simple in design and scalability to large in area growth. Therefore, VHF-PECVD method is good for the high quality of CNW.

A variety of possible applications of CNWs are exciting interest. CNWs have a high density of atomic scale graphitic edges that are potential sites for electron field emission, which might lead to the application in flat panel displays and light sources. So far, a number of publications have reported the field emission properties from carbon nanowalls and related structures (Chuang *et.al.,* 2007, Wang *et.al.*, 2004, Hiramatsu *et.al.*, 2006, Shang *et.al.*, 2002, Obraztsov *et.al.*, 2003, Wu *et.al.*, 2004, Wang *et.al.*, 2004, Srivastava *et.al.*, 2005, Wang *et.al.*, 2005, Wang *et.al.*, 2005, Wang *et.al.*, 2006, Itoh *et.al.*, 2006; Koeck *et.al.*, 2006). Carbon nanowalls were also used as templates for synthesizing mesoporous materials with high surface areas including Au, Cu, Zn, Se, ZnO, TiO_2, SiO_x, SiN_x, and AlO_x (Wu *et.al.*, 2004; Yang *et.al.*, 2002; Wu *et.al.*, 2002; Wang *et.al.*, 2008). Recently, electrochemical and charge/ discharge properties of carbon nanowalls were studied for the application as electrodes of batteries and electrochemical sensors (Giorgi *et.al.*, 2007; Luais *et.al.*, 2009; Tanaike *et.al.*, 2009). Furthermore, since carbon nanowalls essentially consist of graphene sheets, they are expected to have high mobility and large sustainable current density. Therefore, carbon nanowalls are considered for the use in nanoscale electronic devices. Recently, an electrical conduction properties of carbon nanowalls as a bulk film have been reported (Takeuchi *et.al.*, 2008; Takeuchi *et.al.*, 2010; Teii *et.al.*, 2009). These researches are to exploit the potential of graphene and to develop next-generation electronic devices using carbon nanowalls has just begun.

In conclusion, the understanding of growth mechanism model of carbon nanostructures is proven beneficial in order to improve the growth properties for different application. In addition, the documentation of CNW using VHF-PECVD method is less to be found. Therefore, this research will provide knowledge for the growing of CNWs.

1.2 Problem Statement

The controlled synthesis is important to fabricate high quality graphene films with desirable characteristics for specific application. Other methods had been developed in the past decade, however the quality of the film was hardly met with requirements of the application. VHF-PECVD method is the most promising technique for growth of CNWs due to its low substrate temperature, scalable and with better controllable process. The problems detects in controlling parameters are synthesis temperature, plasma sources, the effect of the gas ratios, influence of catalyst, and operating pressure. By controlling the growth parameters of CNWs, it is expected to obtain different qualities of the nanowalls produced from the experiment. As the CNWs properties can be varied with respect to the parameters set up, the change in the properties of these nanowalls can be tailored for specific application. Very high frequency 150 MHz plasma VHF-PECVD has advantages compare to RF plasma (13.56 MHz) in conventional PECVD, including higher plasma excitation frequency leading to better quality films. Therefore, 150 MHz VHF-PECVD is special developed to fabricate the nanowalls. With all the advantages possessed in PECVD method it is possible to produce high quality CNWs in industrial scale. To date, very few researchers had investigated the optical properties of CNWs. The morphologies, structural and optical properties of CNWs will be obtained using spectroscopic technique.

1.3 Research Objectives

The objectives of this research are:

i. To synthesize catalyst-free CNWs by using a 150 MHz VHF-PECVD system.

ii. To determine the optimum synthesis parameters of the catalyst-free CNWs.

iii. To characterize the morphology, structural and optical properties of the catalyst-free CNWs.

1.4 Scope of Research

In order to achieve the objectives, the research has been divided into several scopes which are:

- The growths of catalyst-free CNWs film were done by 150 MHz VHF PECVD method. Various synthesis parameters were optimized to produce CNWs with desired characteristic such as the effect of temperature (650-780°C), the effect of RF power (10-40 watt), and the effect of CH_4 flow-rate (10-40sccm).

- For direct observation of nanowalls height, thickness, and structure of CNWs, the field emission scanning electron microscopy (FESEM) was used. For elemental identification such as the presence of contaminants in the sample, it was determined using electron dispersive X-ray spectroscopy (EDX). The structure and chemical composition of CNWs were characterized using RAMAN spectroscopy and Fourier Transform Infrared (FTIR) Spectroscopy.

The observation of the optical properties of CNWs were analysed using UV-Vis–NIR Spectrophotometer and Photoluminescence Spectroscopy, respectively.

1.5 Significance of Research

The aim of this research is to investigate the controllable growth of CNWs that produce a high quality nanowall with tailored characteristics for specific applications. This research is fundamentally important to provide the information for researchers who is interested pursuing a study of CNWs by exploring the correlation between the effect of variation growth parameters on morphologies and optical properties of the catalyst-free CNWs. Appropriate growth parameters that were obtained can be used to grow CNWs for specific applications which may lead to commercial application based on their unique properties.

1.6 Thesis Outline

This thesis is divided into five chapters. Chapter 1 is the introduction, background of study, the problem statement, objectives, scope of studies and significance of the research as well as the thesis outline. Chapter 2 will focuses on an extensive review of CNWs. Its discovery and history, the different forms of carbon, the growth methods, properties and application of CNWs are reviewed. In this chapter also, some characterization technique used to analysis CNWs were explained in detail. Chapter 3 cover all experiment work, the CNWs synthesis by VHF-PECVD method, sample preparation, the procedure of handling VHF-PECVD system which was used to stimulate the synthesis condition and measurement techniques and the

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