INVESTIGATION ON MORPHOLOGY AND STRUCTURAL PROPERTIES OF 2D CARBON NANOSTRUCTURE GROWN VIA 150 MHz PECVD

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“Demi agama dan negara tercinta”

“For science and humanity”

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ABSTRACT

A 150 MHz very high frequency plasma enhanced chemical vapor deposition (150 MHz VHF-PECVD) system was utilized to fabricate two-dimensional carbon nanostructure from the mixture of CH_4 and H_2. Morphology and structural properties of the grown nanostructure were investigated by means of microscopic imaging, Raman spectroscopy and X-ray diffraction technique. FESEM imaging had revealed two different carbon nanowalls (CNW), namely wavy-like and dense structure. A significant change in the film density and wall size were observed when H_2 flow rate and substrate temperature were varied. It was found that a suitable intermixing of H_2 and CH_4 is necessary for synthesizing good quality CNW. A limited or excessive amount of H_2 flow produced CNW having high defects density and poor surface coverage due to variation in the concentration of H radicals. In addition, a drastic change in film morphology was observed at growth temperature between 750 °C to 850 °C due to high rate of surface reactions. The growth of CNW was found to be more efficient at smaller electrode spacing due to better flux of hydrocarbon radicals towards the substrate surface. Typical characteristics of CNW were observed from strong D band, narrow bandwidth of G band and single broad peak of 2D band of Raman spectra indicating the presence of disordered nanocrystalline graphite structure with high degree of graphitization. The occurrence of strong peak at [002] plane with interplanar distance of 0.34 nm confirmed the growth of 2D highly graphitized CNW. It can be concluded that a capacitively coupled 150 MHz VHF-PECVD is a promising alternative technique for CNW fabrication due to its capability to dissociate CH_4 to CH_x and H radicals more efficiently.

ABSTRAK

Satu sistem pengendapan wap kimia berfrekuensi sangat tinggi 150 MHz, telah diguna pakai untuk menghasilkan karbon berstruktur nano dua dimensi daripada percampuran gas CH_4 dan H_2. Ciri permukaan serta sifat struktur nano yang tumbuh telah dikaji menggunakan teknik pengimejan mikroskop (FESEM), spektroskopi Raman dan teknik pembelauan sinar X. Imej FESEM telah mendedahkan dua jenis sintesis tembok nano karbon (CNW) yang berlainan, iaitu berombak dan tumpat. Perubahan ketumpatan saput dan saiz tembok yang ketara telah diperoleh semasa pertumbuhan pada kadar aliran H_2 dan suhu substrat yang berbeza. Didapati, percampuran gas yang sesuai di antara H_2 dan CH_4 adalah perlu bagi menghasilkan sintesis CNW yang berkualiti. Kadar aliran H_2 yang terhad atau berlebihan akan menghasilkan saput CNW yang berketumpatan kecacatan tinggi serta kawasan liput permukaan yang buruk akibat daripada perubahan kepekatan radikal H. Pada suhu pertumbuhan antara 750 °C ke 850 °C, permukaan saput telah mengalami perubahan drastik akibat daripada kadar tindak balas permukaan yang tinggi. Pertumbuhan CNW didapati lebih cekap pada jarak elektrod yang dekat, disebabkan oleh aliran fluks radikal hidrokarbon kepada permukaan substrat yang lebih elok. Ciri-ciri khusus spektra Raman bagi CNW yang telah diperhatikan iaitu keamatan jalur D yang tinggi, lebar jalur G yang sempit dan puncak 2D berjalur lebar, membuktikan kehadiran struktur nano-hablur grafit yang bercelaru dengan darjah penggrafitan yang tinggi. Kemunculan puncak satah [002] yang tinggi dengan jarak antara satah 0.34 nm, mengesahkan kewujudan struktur grafit dua dimensi. Kesimpulannya, sistem pengendapan wap kimia berfrekuensi sangat tinggi 150 MHz, merupakan satu kaedah alternatif yang memberansangkan bagi pertumbuhan CNW hasil daripada kemampuannya untuk menguraikan CH_4 kepada radikal CH_x dan H dengan lebih berkesan.

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LIST OF ABBREVIATIONS

0D	-	Zero dimensional
1D	-	One dimensional
2D	-	Two dimensional
2D-CN	-	Two dimensional carbon nanostructures
AFM	-	Atomic force microscopy
ASTex	-	Applied Science and Technology Inc.
CCD		Central composite design
CCP	-	Capacitively coupled plasma
CNF	-	Carbon nanoflakes
CNR	-	Carbon nanorods
CNS	-	Carbon nanosheets
CNT	-	Carbon nanotubes
CNW	-	Carbon nanowalls
CVD	-	Chemical vapor deposition
DC-PECVD	-	Direct current plasma enhanced chemical vapor deposition
DLC	-	Diamond-like carbon
EBE-PECVD	-	Electron beam excited plasma enhanced chemical vapor deposition
FC	-	Filamentous carbon
FESEM	-	Field emission scanning electron microscope
FET	-	Field effect transistor

GIXRD	-	Grazing incidence x-ray diffraction
HFCVD	-	Hot filament chemical vapor deposition
ICP	-	Inductively coupled plasma
LR	-	Laboratory grade
MFC	-	Mass flow controller
MPECVD	-	Microwave plasma enhanced chemical vapor deposition
MSDS	-	Material safety data sheet
MWCNT	-	Multiwall carbon nanotubes
nc-graphite	-	Nanocrystalline graphite
NIRIM	-	National Institute of Research of Inorganic Materials, Japan
PECVD	-	Plasma enhanced chemical vapor deposition
RF	-	Radio frequency
RF-CCP	-	Radio frequency capacitively coupled
RI-CCPCVD	-	Radical injection capacitively coupled plasma enhanced chemical vapor deposition
RF-ICP	-	Radio frequency inductively coupled plasma
sc-Si	-	Single crystal Silicon
SEM	-	Scanning electron microscope
SWCNT	-	Single wall carbon nanotubes
TEM	-	Transmission electron microscope
VHF-PECVD	-	Very high frequency plasma enhanced chemical vapor deposition

LIST OF UNITS AND SYMBOLS

cm	-	Centi-meter (unit of length)
mm	-	Mili-meter
nm	-	Nano-meter
μm	-	Micro-meter
A/cm^2	-	Ampere per centimeter square (unit of current density)
min	-	Minutes
s		Seconds
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)
°	-	Degree (unit of angle)
°*C*	-	Degree celcius (unit of temperature)
W	-	Watt (unit of power)
Ω	-	Ohm (unit of electrical resistance)
%	-	Percentage
MHz	-	Mega-Hertz (unit of frequency)

GHz	-	Giga-Hertz
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
Co	-	Cobalt catalyst
Cu-Kα	-	Copper-K alpha X-ray source
E_D	-	Electrode distance
Fe	-	Iron catalyst
G_t	-	Growth time
H	-	Hydrogen atom or radicals
H_2	-	Hydrogen gas
I_D	-	Intensity of D band
I_G	-	Intensity of G band
I_{2D}	-	Intensity of 2D band
I_D/I_G	-	Intensity ratio of D to G band
$I_{D'}/I_G$	-	Intensity ratio of D’ to G band
I_{2D}/I_G	-	Intensity ratio of 2D to G band
MnO_2	-	Manganese Oxide
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
T_s	-	Substrate temperature
$W_{D'}$	-	Bandwidth of D band
W_G	-	Bandwidth of G band
W_{2D}	-	Bandwidth of 2D band
λ_α	-	Wavelength of X-ray beam

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CHAPTER 1

INTRODUCTION

1.1 Section Overview

This thesis presents the investigative report on two-dimensional carbon nanostructure (2D-CN) fabrication and structural characterizations; focusing on carbon nanowalls (CNW), grown by very high frequency RF plasma enhanced chemical vapour deposition (VHF-PECVD). The thesis starts with a brief review of the most popular one-dimensional (1D) and 2D carbon nanostructure and their potential applications, characteristics of graphite-based nanomaterial, bottom-up approach of depositing thin film for carbon nanostructure, structural properties characterization, experimental results and finally the conclusion and suggestions. Toward the end of this chapter, the aim and outline of the thesis will be discussed.

1.2 Background of the Study

1.2.1 Brief Description of Renowned Carbon Nanostructures

Low dimensional carbon material popularity has been increased since the groundbreaking discovery by Iijima (1991), where he first reported on the growth of helical graphitic microtubules or as nowadays widely known as carbon nanotubes (CNT), which has been the pioneer of bottom-up fabrication of carbon nanostructures. Thirteen years later, another great experimental discovery by Novoselov *et al.* (2004) regarding the electrical properties of graphene has made carbon nanostructure as the most promising material for future application in nanoelectronics, photovoltaic and energy storage. Since then graphite-based material has been in the highlight and intensively studied.

Carbon nanostructures are originated from manipulation of graphene honeycomb atomic lattice, expressed in various shapes and dimensions. 1D carbon nanostructures such as CNT, filamentous carbon (FC) and carbon nanorods (CNR) are labeled as 1D because of their one-direction growth (Hiramatsu and Hori, 2010). For example, CNT is composed of manipulation of graphene sheets into rolled or hollow cylindrical form. A single wall CNT (SWCNT) is only consists of one roll of graphene sheet, meanwhile a multi-wall CNT (MWCNT) possesses two or more rolled-graphene sheets to form tubular graphitic structure.

A two-dimensional carbon nanostructures (2D-CN) such as carbon nanosheets (CNS), carbon nanoflakes (CNF) and carbon nanowalls (CNW) are a self-organized of stacked flat graphene sheets forming graphitic building block of walls or petal-like structure. The structure exhibits sharp edges with high aspect ratio that is typically in the range of few nanometer to tens of nanometer. For example, a CNW is composed of combination of planar graphene layers, stacking towards each other to form almost vertical graphitic walls. The sharp edges of the wall determine its aspect ratio.

1.2.2 General Characteristic and Application of 1D and 2D Carbon Nanostructures

Bulk carbon material has contributes toward many industries such as polymer, composite, firefighting, electrochemical sensors and energy production. As the rapid emergence of nanotechnology, there has been a lot of interest in producing carbon nanomaterials, which characteristics and properties are expected to surpass their bulk material. For example, diamond has been considered as the hardest bulk material on earth, indebted to its sp^3 carbon units of zinc-blende atomic lattice. However, CNT is predicted to overtake diamond in hardness (Kumar and Ando, 2010), as it possesses sp^2 carbon bond units of honeycomb lattice, which is approximately 56 times stronger than steel wire. In summary, graphite-based nanostructures exhibit interesting mechanical, physical and chemical properties due to the existence of honeycomb crystal lattice.

1D and 2D carbon nanostructure are blessed with excellent mechanical properties, high carrier mobility, large and sustainable current density and high absorption of light in the visible range. Most of these features are highly demanded in nanoelectronics, electron field emission, and blackbody-like coating. For example, the exploitation of excellent mechanical and electrical properties of CNT has proven to be beneficial in scanning probe microscopy. In a report by Ye *et al.* (2004), they had successfully fabricated a large-scale production of CNT cantilevers for atomic force microscopy (AFM) imaging with good image capturing characteristics. Besides that, high current density of CNT (10^9-10^{10} A/cm^2) has made it possible to adapt with the continual decreasing size of Si integrated circuits. This has been proven by the fabrication of CNT as field effect transistors (FET) as reported by Wind *et al.* (2002);

Javey *et al*. (2004). In pursuit of producing a high efficiency solar cell, high light absorption material is needed to collect maximum amount of solar energy. SWCNT forest has been proven to behave like a blackbody material, as it is capable of absorbing a wide range of light. Works by Mizuno *et al*. (2009) have shown that vertically aligned SWCNT forest is capable to absorb light of wide spectral range (0.2 – 200 μm).

As for 2D-CN, its application may vary depending on its morphology and film quality. According to Hiramatsu and Mori (2010), 2D-CN with sharp edges, aligned and medium spacing of walls are demanded for application in field emission. In contrast, high-density film with less aligned walls structure is more suitable for gas storage application. In a report by Krivchenko *et al*. (2013), densest CNW film with minimal edges size possessed the best optical absorption behavior and they exhibit higher light absorption by one order of magnitude compared to CNT forest. On the other hand, the most promising application for 2D-CN such as CNW is to be employed as templates for growth of nanostructure and this has been proven fruitful for application in energy storages devices. For example, in the works of Hassan *et al*. (2014), they had managed to fabricate MnO_2 thin film with CNW/Ni as templates and found that dense and sharp edges CNW film with minimal defects lead to fast electron and ion transport and stable electrochemical cyclic activity thus providing a unique capacitive behavior.

1.2.3 General Approach and Bottom-up Synthesis of Carbon Nanostructures

Conventional thin film deposition method such as CVD has been renowned of its versatility in fabricating numerous nanostructures including carbon. There have been numerous reports regarding the growth of carbon nanostructure using modified CVD method such as DC-PECVD, RF-PECVD, Microwave PECVD (MPECVD) and electron beam excited PECVD (EBEPECVD). Typically, precursor gas such as methane and acetylene are employed as the carbon source. For the growth of CNT, arc-discharge method and catalytic thermal CVD have been commonly employed in tremendous reports while PECVD is often employed in purpose to increase deposition rate and to lower the growth temperature. However, the history of 2D-CN growth is involved with accidental event prior to fabricating CNT. The earliest report on 2D-CN can be found in the work of Ando *et al*. (1996), where he observed both CNT and other petal-like graphite sheets using hydrogen arc discharge method. Meanwhile, in 2002, Wu *et al*. (2002) had reported the growth of CNW on catalyzed substrates using MPECVD. This can be considered as the first report to use the term "carbon nanowalls". Currently, 2D-CN is fabricated by using various PECVD with modification, for example PECVD with hydrogen radical injection.

1.2.4 Motivation to Conduct Research on 2D Carbon Nanostructures

As has been briefly reviewed previously, 2D carbon nanostructures exhibit unique mechanical, physical and chemical properties. Hence, intensive research on its fabrication method and film properties can be fruitful as a stepping-stone toward providing alternative in many fields of applications such as renewable energy and nanoelectronics.

To date, the understanding regarding growth mechanism of 1D and 2D carbon nanostructures are still premature. For 1D carbon nanostructure such as CNT, two growth mechanisms; i) tip-growth model and ii) base-growth model have been widely accepted, however these growth mechanisms are only applicable for CNT growth on catalyzed substrate. Still, there have been reports on CNT growth on non-catalyzed substrate (Rumelli *et al*., 2011.). For 2D-CN, there have been a number of reports on its growth mechanism and is proven direct yet random. Briefly, the growth of 2D-CN is initialized with the nucleation stage of precursor gas followed by random assembly of nanoflakes on top of agglomerated nanoislands (Kondo *et al*., 2009).

As conclusion, the understanding on growth mechanism model of carbon nanostructures is proven beneficial in order to further control and manipulate their growth properties for different application. It is hoped that the result of this study can be used to provide clarification on 2D-CN growth properties. Furthermore, the fabrication of 2D-CN using VHF-PECVD is less to be found, thus this study will help to provide a report on the ability of VHF-PECVD to grow CNW. It must be noted that VHF-PECVD is simpler to setup compared to radical injection PECVD and MPECVD.

1.3 Statement of Problems

All previously mentioned superior physical properties of 2D-CN however, currently exhibits some difficulties especially in material preparation and processing requirement, which are unique compare to the well-established Si processing. To date very few researchers have achieved to produce CNW with tunable morphology since its application is highly dependent on film density and structural arrangement of the walls. Besides that, current researches on the fabrication of CNW often employed a highly modified PECVD system such as MPECVD and capacitively-coupled PECVD with hydrogen radical injection. The conventional PECVD with 13.56 MHz RF plasma source is simpler to assemble compared to MPECVD and PECVD with hydrogen radical injection, which employed a two-stage plasma source to operate.

1.4 Objectives of Study

The objectives of this study are as followed;

1) To optimize the growth condition of CNW by varying H_2-to-CH_4 gas flow rate ratio, substrate temperature, electrode separation and deposition time.

2) To determine the influence of H_2 flow rate percentage, substrate temperature and electrode separation on CNW growth.

3) To characterize the surface morphology, crystallinity and degree of graphitization of grown CNW.

1.5 Scope of Study

In order to meet the research objectives, the experimental works must be thoroughly outlined and highlighted. The focus of this research can be categorized into two different components, which includes the fabrication of CNW using VHF-PECVD and characterization of its surface morphology and structural properties.

In the fabrication of CNW, growth parameters played a crucial role in determining the film quality. Parameters investigated in this study are summarized in Table 1.1.

Table 1.1 : Summary of chosen experimental parameters.

No.	Parameter	Range/ value	Unit
1.	CH_4-to-H_2 flow rate ratio	17:0 – 17:20	Standard cubic centimeter, (sccm)
2.	Substrate temperature	700 - 850	Celcius, (°C)
3.	Electrode separation	25 – 55	Milimeter, (mm)
4.	RF power	25	Watt, (W)

Meanwhile, the substrates chosen for this study were quartz glass and single crystal Si. Typically, the growth of CNW does not require the presence of catalyst, however in this study some samples will be equipped with thin film of Ni catalyst in order to see its influence on film morphology.

For characterization of CNW film, properties such as; i) surface morphology, ii) crystallinity, and iii) degree of graphitization were chosen. In order to study the surface morphology, microscopic imaging such as field emission scanning electron microscopy (FESEM) was employed. The crystallinity and structural properties of film such as defect and stacking of graphene layers were investigated using grazing incidence x-ray diffraction (GIXRD) and Raman spectroscopy.

Finally, the growth parameters and structural characterization were correlated in order to determine the optimum growth condition of CNW using VHF-PECVD. It will also reveal the ability and feasibility of 150 MHz VHF-PECVD in synthesizing 2D carbon nanostructure with tunable morphology.

1.6 Significance of Study

As has been mentioned earlier in this chapter, carbon nanostructures exhibit unique and promising material properties for future application in variety of fields. It is hoped that this study will bring more enlightenment regarding the fabrication technique and film properties of CNW.

To date, most fabrication approach of CNW involve highly modified and complex system of PECVD. Thus, this study is hoped to evaluate the potential of simpler PECVD system (VHF-PECVD) to fabricate CNW. There are also reports on the utilization of high frequency PECVD such as in the works of Dikosnimos *et al*. (2005), however to the best of our knowledge, there are no reports on CNW film grown via 150 MHz VHF plasma source. Microwave PECVD can be classified as ultrahigh frequency plasma source at typical value of 0.915 and 2.45 GHz but it always involves the use of magnetron, which require very high voltage to operate.

In most cases, the growth of CNW does not require any catalyst, thus it is less time-consuming procedure, as there is no substrate and surface plasma treatment needed. Furthermore, it has become possible to grow CNW in various type flat surface such as Si wafer, stainless steel and glass. Another important feature of CNW is its blackbody-like behavior. Combination of both features will provide the solar cell and energy storage industry an alternative of new coating material in purpose to improve solar cell efficiency.

1.7 Thesis Layout

This thesis consists of five chapters. Each of the chapters will be briefly discussed and they are interrelated to each other bounded by the scope of study.

Chapter 1 deals with the overview of 1D and 2D carbon nanostructures, and their potential applications, recent fabrication technique and motivation to provide the need of study by highlighting its drawbacks. Therefore, an alternative is proposed concerning the specific problem, which has been addressed in the objectives of the study.

Chapter 2 is a detail review on the types of morphology of CNW and recent reports that cover recent fabrication technique and its influence on growth properties of CNW film. It also discusses the experimental results of recent literature regarding its structural properties. The parameters that affect the process were addressed in this chapter.

Chapter 3 describes the methods, technique and characterization preferred to be implemented in this study. Samples were taken for analysis and all the analytical methods are described in this chapter.

Chapter 4 is the full result of this study. The parameters that contribute and give impact to the study will be discussed. Each of the result will be transformed into simplified graphical representation for further clarification and discussion..

Chapter 5 is the conclusion obtained from the study. It gives an insight on how the objectives have been met. The chapter ends with suggestions that were made for future research.

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