UNIVERSITI TEKNIKAL MALAYSIA MELAKA

COMPARATIVE STUDY OF ELECTRONIC PROPERTIES IN PRISTINE AND SI-DOPED SINGLE-WALLED CARBON NANOTUBE AS GAS SENSOR: A FIRST PRINCIPLE STUDY

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment to the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

……..

(Dr. Mohd Asyadi Azam bin Mohd Abid)

ABSTRAK

Nanotiub karbon berdinding tunggal dan silikon pendopan nanotiub karbon berdinding tunggal telah disiasat sebagai salah satu bahan untuk peranti pengesan gas. Gas yang telah dipilih ialah karbon dioksida, oksigen dan metanol disebabkan oleh penggunaan yang meluas dan dikawal dalam penggunaan dalam sector industri. Penjerapan dan ciri-ciri elektronik telah disiasat keatas nanotube karbon berdinding tunggal yang tulen dan yang telah didopan keatas reaksi gas kepada dinding nanotiub karbon berdinding tunggal. Semua pengiraan dijalankan menggunakan kajian prinsip pertama berteraskan teori fungsian ketumpatan (DFT) dimana telah dilaksanakan dalam kod komputer CASTEP and DMol3. Untuk pengoptimuman geometri, telah mengunakan korelasi pertukaran anggaran-anggaran fungsian seperti Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) supaya struktur menjadi tepat. Dengan menggunakan GGA, didapati bahawa ketepatan pengiraan sebanyak 80% ke 90% pada keseluruhan hasil. Dari segi tenaga serapan menunjukkan O_2 dan CO_2 mempunyai serapan yang lemah terhadap nanotube berdinding tunggal namun CH_3OH dengan kadar -0.61 eV dan gas yang terletak pada silikon pendopan nanotiub karbon berdinding tunggal menunjukkan tenaga serapan yang tinggi menghasilkan reaksi dengan kadar diantara -1.6 eV ke -3.99 eV. Untuk pengiraan ciri-ciri elektronik, hasil menunjukkan penambahan state berdekatan valance band dan mengurangkan jurang band sebanyak 0.5 eV daripada strakture original nanotube berdinding tunggal sebanyak 0.6 eV sementara DOS menunjukkan jenis-P semikonduktur menghasilkan lebih sensatif gas sensor ketika diekposkan dengan gas. Oleh itu, dengan pencarian ini mampu menaikan usaha untuk mengoptimumkan pengunaan gas sensor dan akan menyumbang kepada lebih sensatif gas sensor.

ABSTRACT

A pristine single-walled carbon nanotube (SWCNT) and silicon-doped SWCNT have been investigated as materials for gas sensor. The gases that had been chosen were carbon dioxide, oxygen, and methanol due to their widely use and controlled in industrial sector. Adsorption and electronic properties were investigated on the pristine and doped SWCNT upon the gas reacted to SWCNT wall. All the calculation were performed using a first principle study base on density functional theory that has been implemented in CASTEP and DMol3 computer code. For geometry optimization, exchange correlation functional approximations such as Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) have been utilized in order to get accurate structural information. Using GGA showing improvement in accuracy of data by 80% to 90% in overall calculation. In term of adsorption energy indicates that the O_2 and CO_2 are weakly adsorbed on the pristine SWCNT but CH_3OH with value of -0.61 eV and all other gases attached on Si doped SWCNT showing higher amount of adsorption energy that promote to chemisorption reaction with value range of -1.6 eV to -3.99 eV. As the electronic properties been calculate, the result indicate there is additional state produce at valance band and reducing the band gap structure in silicon-doped SWCNT of 0.5 eV from the original pristine structure of 0.6 eV while DOS showing a p-type semiconductor properties producing a more sensitive electronic properties upon doping and exposure of gases. Thus, these finding will be able to gear up efforts in optimizing the usage of gas sensor and hence will substantially contribute to the more sensitive gas sensor.

DEDICATION

To everyone that contributes to this research, my family and my friend that has been helping me all along.

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1D	-	One dimensional
2D	-	Two dimensional
3D	-	Three dimensional
μm	-	Micrometer
$\hat{H}$	-	Hamiltonian operator
Ψ	-	Wavefunction
Å	-	Angstrom
a	-	lattice vectors
B	-	Boron
BZ	-	Brillouin-zone
C	-	Carbon
CASTEP	-	Cambridge serial total energy package
C_h	-	Chiral vector
CB	-	Conduction band
CH_3OH	-	Methanol
CNT	-	Carbon nanotube
CO	-	Carbon monoxide
CVD	-	Chemical vapor disposition
DFT	-	Density functional theory
DFPT	-	Density functional perturbation theory
DMol3	-	Density functional calculation on molecules
DOS	-	Density of state
E	-	Energy
e	-	Electron charge
E_{ad}	-	Adsorption energy
eV	-	Electron volt
FFT	-	Fast Fourier transform
GGA	-	Generalized gradient approximation

HCP	-	High performance computer
IR	-	Infrared
LDA	-	Local density approximation
NH_3	-	Ammonia
NO_2	-	Nitrogen dioxide
nm	-	Nanometer
M	-	Electron mass
MS	-	Materials studio
MWCNT	-	Multi-walled carbon nanotube
O_2	-	Oxygen
P	-	Momenta of ions
PC	-	Personal computer
PW91	-	Perdew and Wang
r	-	Radius
r_c	-	Cut-off radius
SCF	-	Self consistence field
Si	-	Silicon
SWCNT	-	Single-walled carbon nanotube
USP	-	Ultra-soft pseudopotential
VB	-	Valance band
Viz.	-	Visualizer
WDA	-	Weight density approximation
XC	-	Exchange-correlation
Z	-	Charge of ion

CHAPTER 1
INTRODUCTION

1.1 Background Study

Nowadays, gas sensors are becoming more essential measurement for the used in industries and factories as well as in the daily life. Many gases can be a perfect example of a gas that can be harmful such as carbon monoxide, carbon dioxide and many others. Due to this causes, detectors for this gas can be found in many mass market retailers and industries across the country. As a results, gas sensors are being extensively studied to develop a sensitive, low cost and reliable gas sensor.

Basically, chemical gas sensor is well defines as a device that is able to change the physical properties upon exposure to gas molecules through electrical conductance. An electrical signal is measured upon the change in these properties and the results are then used to detect the gas molecules. Fast response time and high accuracy are the two basic requirements for gas sensors. According to Kerotocenkov (2013), the size, cost and weight are the main constraints along producing sensor with capability to measure the physical properties over a certain lifetime. In contrast, commercially market available for gas sensors have advantages in lower cost, smaller size and easy to operate. Typical gas sensors can be from in a variety of size micrometers to centimeters while the size can be reduced due to rapid large scale ups of such productions (Yamazoe, 2005). These all make these gas sensors viable for real time in situ environments. Meanwhile, the

major drawbacks for gas sensors include stability, sensitivity, selectivity, and reproducibility which could render these gas sensors unsuitable for long term usage.

Nanotechnology is known as any process or product that has sub micrometer dimensions. Since 1990s, there is a rapid growth in research interest of nanotechnology including increasing in high performance of nanomaterials and nanoscale electronic devices. (Pandyan, 2012). The discovery of carbon nanotubes (CNTs) has been attracted considerable attention since they have a wide range of applications in nanometer-scale electronic devices. Furthermore, carbon material in sensor technology becoming an ideal component, since they have a very good sensitivity on sensing with interesting electronic properties of the materials (Roberts et al, 2009). As a result, recent advancements in nanotechnology have provided opportunities to improve sensor performances in detecting gases dramatically. Considerable interests have been on new room temperature operated gas sensing materials. Due to their ability to change the electrical properties upon exposure to the gas molecule and high surface, CNTs have been a promising as new gas sensing material combining with outstanding properties which include high performance, fast respond upon exposure of gas and wide selectivity of gases that able to be detected (Jung et al, 2014). Therefore, a huge effort in research has been carried out in new gas sensors as the demand of gas detection technologies is increased. It is indeed not surprising to see the sensor research community as a beneficiary due to advanced nanomaterial developments as carbon nanotubes have been one of the mostly studied nanomaterial.

Quantum calculations using first principle study base on the density functional theory (DFT) provide a great opportunity to prescribe the initial and the fundamentals properties in materials. Furthermore, the atomic view can be accurately visualized in detail. Besides that, the first principle calculations require less empirical data with cost efficient comparing to the experiment laboratory work which will help in term of reasonable and affordable in large scale material design.

The main focus of this study is to investigate and understand the pristine and doped zigzag (*8, 0*) single-walled carbon nanotube (SWCNT) reacted toward gas adsorption. The zigzag (*8, 0*) SWCNT was choosen because, according to Iijima and Ichihashi (1993), the (*8, 0*) CNTs were dominant during synthesized and having a semiconductor nature. In addition, the gasses consists of O_2, CO_2, and CH_3OH that will react with pristine SWCNT, but the doping system in SWCNT anticipated to enhance the adsorption energy as well as the electronic properties upon adsorption of gases which will promote an impact in sensitivity of the gas sensor technology. Furthermore, the gases were chosen due to the wide range of industrial application and some of them having human and environmental issues.

1.2 Problem statement

There have been a high interest studies toward gas sensing application using CNT. However, there are less fundamental understanding in the interaction behavior classes of gas molecules (O_2, CO_2, and CH_3OH) with pristine CNT and doped CNT system (Zanolli et al., 2011). Ironically, there are only investigation on the amount of gas that can be adsorbed by the CNTs but no identification on binding distance and stable position of the gas reacted toward the CNTs. Therefore, upon understanding the sensitivity of the gas molecule adsorption, the geometry and adsorption behavior (adsorption energy) becoming essential. According to G. Guo et al. (2007), pure CNTs are sensitive only toward gas molecules such as NO_2, SO_2, and O_2 which have strongly chemical interaction with CNTs. Thus, it is highly recommended to find the effective ways to improve the sensitivity of CNTs upon other molecules, in particular industrial application as well as the human and environmental effects gases. Furthermore, pristine SWCNT having a weak Vander wall forces and it cannot detect some of gas molecules such as carbon monoxide and ammonia (Pandyan et al., 2012).

It has been widely studied that the electronic properties of CNTs having a semiconducting nature and very sensitive to only certain gases. Moreover, the range of gases CNTs sensors can be detected are limited to gas molecules that possess large binding energies and charge transfers toward nanotube (Wang and Yeow, 2009). According to Adjizian et al. (2014), the special characteristics of CNT due to they possess high surface area to interact with gases and the electrical conductivity change upon the gas adsorption at room temperature. A promising approach to enable single-walled carbon nanotubes (SWCNTs) to detect gas molecules is by doping (heteroatom substitution), when heteroatom impurities are being introduced (such as Silicon) or forming active sites in tube walls, the sensitivity of adsorption on SWCNTs can be improved (Bai et al., 2007).

Moreover, the use of different doping atom (Si) will produce different electrical properties for semiconductor SWCNT that also help in producing a sensitive gas sensor, but there are limited understanding on the changing in electronic properties of doped CNT (Llobet, 2013). Furthermore, the electronic properties of gas adsorbates upon molecule adsorption producing different electronic properties with different type of gas interaction. The effect of the electronic properties through doping and gas adsorption can be observed in the change in the electrical resistance. Indeed, electronic charge transfer between the gas molecule and the doped CNT will affect the position of the Fermi energy and effect the conductivity of gas detection (Zanolli et al., 2011). The need to understand the adsorption behavior and the electrical properties of doped SWCNT upon gas adsorption is worth it to study in suggesting the good sensitivity of gas sensor as it will show the electron charge transfer concepts upon adsorption of gases molecule.

1.3 Objectives

The main objectives of this project are:

i. To understand the fundamental insight into the molecular interactions between common gaseous adsorbates pristine SWCNT and Si-SWCNT models.

ii. To investigate electronic properties of pristine and silicon doped (*8, 0*) zigzag SWCNT upon gas molecular adsorption.

1.4 Scope

This project will mainly focus on understanding the right adsorption in term of high adsorption energy of these molecules base on the geometrical configuration and structural stability of doped SWCNT. After completing the adsorption energy and geometrical analysis, there are also several measurements need to be account in order to achieve high sensitivity which is electronic properties. Furthermore, from electrical properties involved the study of changing in band structure and density of states using density functional theory based on computational numerical base to achieve the best type of doped SWCNT related to gas sensor application. In order to optimize the structure of pristine and doped SWCNT upon gas adsorption and understanding their electronic properties, DFT theory were executed. Chapter 1 offers an overview to the project by describing the important of SWCNT as gases sensor and explain the basic of using computational as to design a new material base on the quantum theory. Furthermore, the project problem were identified and proposed solutions that need to be gain are established in problem statement. Chapter 2 provides review on SWCNT material as well as Silicon doped SWCNT upon gases molecules. Also, this chapter brief the first principle study of adsorption behavior between pristine and doped SWCNT on exposure to gases molecule will be explained in this chapter. More, DFT also been reviewed in detail starting from Schrodinger equation until energy cut-off for using basis set of plane wave with Local Density Approximate (LDA) and Generalized Gradient

Approximate (GGA) exchange correlation. Chapter 3 describe the methodology on computational and understanding the usage of first principle calculation that been applied in this project. The computational methods setting parameters are shown and well explained to ensure the calculation technique are the most accurate with cut-off energy and convergence the k-point. The structures of pristine SWCNT and doped SWCNT are respectively built by using Material Studio Visualizer. The adsorption energy and electronic properties are perform by using DMol3 and CASTEP computer modules.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

This chapter provides an overview on the basic understanding of carbon nanotube (CNT) and will be discuss in order to understand the molecular structure of the materials. The literature of doping system in CNT and an understanding the nature of gas molecules and adsorption for CNT are also stated with regard to cover the scope of our research. In addition, the density functional theory (DFT) with first principle study and as one of the mathematical and physic tools to investigate the electronic properties of pristine and doped CNT upon gas adsorption are also reported in this chapter.

2.2 The nature of carbon

Carbon is an element having 6 as an atomic number with a symbol C. From the periodic table, the element of carbon belong to the group 14 which is respected having a non-metallic group with a six elections with two of the electron filling the 1s orbital another remaining electron fill the sp^2 for double bonding or sp^3 for single bonding as well as the sp hybrid orbital for triple bonding. According to Zhang (2012), in comparison with different bonding state will introduce into certain structural arrangement in which sp bonding will give rise to one dimensional chain structure, sp^2 bonding will produce planar structure and sp^3 bonding to tetrahedral structure.

The short lived nature of atomic carbon is effect the stability, because of that carbon is stabilized in different molecular configurations with different structures called allotropes. Moreover, the several best allotropes are graphite, nanoform, and amorphous carbon with recent addition of fullerenes and carbon nanotube (D'Souza and Kadish, 2012). The carbon tree family which is shown Figure 2.1 shows that the range in carbon nanoform family of is significantly larger than mention because of unique bonding versatility of carbon.

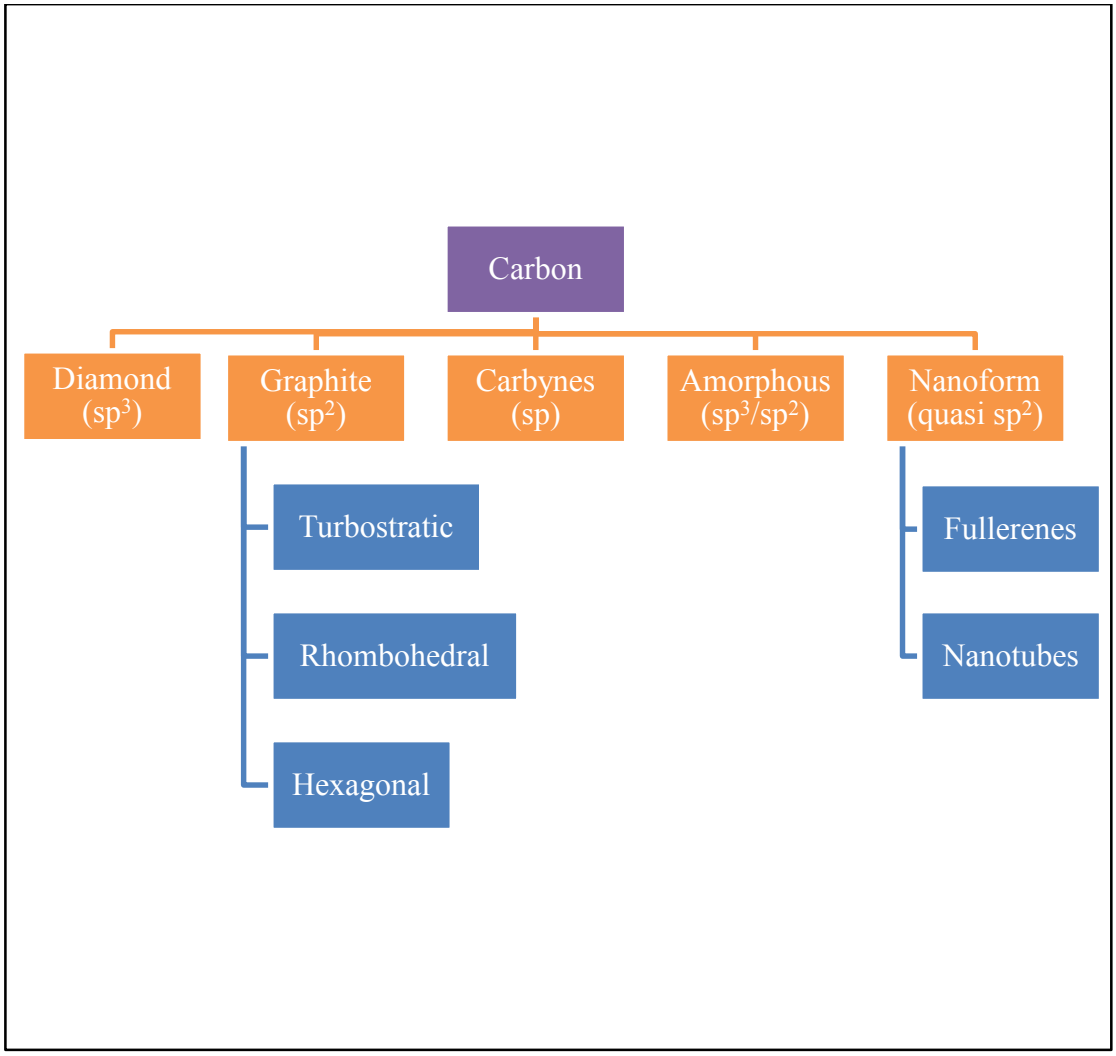

Figure 2.1: Summary of different carbon form