LOW DIMENSIONAL CARBON BASED MATERIALS FOR LOW PRESSURE MEASUREMENT APPLICATION

by

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LIST OF SYMBOLS

SYMBOL	DESCRIPTION	SI UNIT
S	Sensitivity	Pa^{-1}
ΔV	Change in voltage	V
V_{in}	Input voltage	V
ΔR	Change in resistance	Ω
R	Resistance	Ω
R_0	Initial resistance	Ω
$\Delta R/R$	Relative change in resistance	-
I	Current	A
ΔP	Change in pressure	Pa
NLi	Nonlinearity	-
ρ	Resistivity	Ω.m
l	Length	m
A	Area	m^2
w	Width	m
h	Height	m
g	Gauge factor	-
ε	Strain	-
v	Poisson's ratio	-
h_e/h_d	Ratio of electrode finger thickness to diaphragm thickness	-
w_e/g_e	Ratio of electrode width to electrode gap	-
$\Delta\rho/p$	Relative change in resistivity	-
w_0	Maximum deflection	m
σ_{max}	Maximum stress	Pa
P	Pressure	Pa
T	Temperature	K
B	Magnetic field	T
d	Initial thickness	m
MR	Magnetoresistance	-
I_D/I_G	Intensity ratio	-

LIST OF ABBREVIATIONS

0-D	Zero-dimensional
1-D	One-dimensional
2-D	Two-dimensional
3-D	Three-dimensional
CVD	Chemical vapor deposition
PECVD	Plasma enhanced chemical vapor deposition
HFTCVD	Hot filament temperature chemical vapor deposition
IDE	Interdigitated electrode
FEA	Finite element analysis
FESEM	Field-emission scanning electron microscopy
SEM	Scanning electron microscopy
HRTEM	High-resolution transmission electron microscopy
TEM	Transmission electron microscopy
AFM	Atomic force microscopy
MEMS	Microelectromechanical system
NEMS	Nanoelectromechanical system
Si	Silicon
Ge	Germanium
Pt	Platinum
Au	Gold
Ag	Silver
Cr	Chromium
Co	Cobalt
Cu	Copper
Fe	Iron
Ni	Nickel
Mo	Molybdenum
Zr	Zirconium
Ir	Iridium
Ru	Ruthenium
SiNW	Silicon nanowire
3C-SiC	Cubic unit cell-silicon carbide
TCR	Temperature coefficient of resistance
CNT	Carbon nanotubes

SWCNT	Single-walled carbon nanotubes
MWCNT	Multi-walled carbon nanotubes
CNTF	Carbon-nanotube thin film
PDMS	Polydimethylsiloxane
PMMA	Polymethyl methacrylate
PI	Polyimide
CMC	Carbon microcoils
CNF	Carbon nanofiber
SiN_x	Silicon nitride
SiO_2	Silicon dioxide
RIE	Reactive ion etching
MCNP	Monolayer-capped nanoparticles
GO	Graphene oxide
a:Si-H	Hydrogenated amorphous silicon
TiN	Titanium nitride
RF	Radio frequency
NH_3	Ammonia
Ar	Argon
H_2	Hydrogen
C_2H_2	Acetylene
CH_4	Methane
UV	Ultra violet
NP	Nanoparticles
Co-Fe@C NP	Carbon-capped Co-Fe nanoparticles
Au-Fe@C NP	Carbon-capped Au-Fe nanoparticles
RT	Room temperature
RMS	Root mean square
GMR	Giant magnetoresistance

BAHAN DIMENSI RENDAH BERASASKAN KARBON BAGI PENGUKURAN APLIKASI TEKANAN RENDAH

ABSTRAK

Kemajuan dalam sains bahan dan kejuruteraan reka bentuk telah merealisasikan peranti tekanan fleksibel yang sangat peka. Setakat ini, banyak kemajuan pada ciptaan peranti tekanan piezo rintangan berdasarkan bahan berskalar nano yang berfungsi dan struktur diafragma telah ditunjukkan secara meluas di mana perhatian yang besar telah tertumpu kepada peningkatan kepekaan dengan penggunaan bahan berskalar nano yang berfungsi dan pengoptimuman geometri peranti. Namun, pengesanan julat tekanan rendah (<10 kPa) dalam masa nyata dengan kepekaan yang sangat baik kurang dilaporkan oleh pengkajian semasa peranti tekanan piezo rintangan kerana dua sebab yang jelas: (i) kurang eksploitasi bahan berskalar nano yang berfungsi melalui kaedah sintesis yang dikawal dan (ii) penggunaan struktur reka benda diafragma yang konvesional. Sehubungan itu, kajian ini bertujuan untuk membangunkan peranti tekanan piezo rintangan yang fleksibel, terutamanya memberi tumpuan kepada peningkataan tahap kepekaan dengan penggabungan bahan dimensi rendah berasaskan karbon yang baru dibangunkan dan struktur diafragma dengan tatasusunan interdigital elektrod (IDE) untuk memenuhi keperluan aplikasi tekanan rendah. Ciri-ciri baru bahan dimensi rendah berasaskan karbon untuk 0-D nanopartikel berlapisan karbon, 1-D nanotuib karbon dan 2-D filem nipis grafen telah diperkenalkan melalui pengendapan wap kimia (CVD) dan sifat-sifat morfologi dan elektrik telah dicirikan dengan teliti. Sebelum pembuatan peranti, analisa pada ciri-ciri diafragma baru dengan struktur penguat tambah tatasusunan interdigital elektrod (IDE) telah dicapai melalui CoventorWare® menggunakan analisis unsur terhingga (FEA). Kajian parametrik telah dilaksanakan untuk semua simulasi untuk menilai pengaruh parameter geometri ke atas ciri-ciri penting yang berkaitan. Seterusnya, dua langkah penting yang terlibat dalam pembangunan peranti tekanan seperti penyepaduan tatasusunan interdigital elektrod (IDE)

pada substrat fleksibel dan kaedah pemindahan bahan-bahan dimensi rendah berasaskan karbon juga telah ditunjukkan. Berdasarkan keputusan pencirian bahan dimensi rendah berasaskan karbon, kesamaan dan keboleh talaan morfologi bahan-bahan yang dihasilkan pada konfigurasi yang berbeza bawah kawalan telah dicapai dengan sifat-sifat elektrik yang sangat baik. Kajian teknikal yang diketengahkan termasuk pertunjukkan kejayaan ciri baru dengan model mekanisma pada lapisan karbon pada 0-D nanopartikel, pembentukan pertumbuhan mendatar pada 1-D nanotuib karbon dan peningkatan kecacatan pada 2-D filem nipis grafen dengan kaedah CVD. Untuk keputusan pencirian elektromekanik, ia telah menunjukkan bahawa rekaan peranti tekanan fleksibel yang digabungkan dengan bahan-bahan dimensi rendah berasaskan karbon boleh dikendalikan secara berkesan pada tekanan di bawah 10 kPa dengan kepekaan yang tinggi, kelinearan yang tinggi dan faktor tolok yang tinggi ke atas tindak balas kepada perubahan kecil dalam tekanan. Kepekaan peranti yang direka dengan 0-D nanopartikel berlapisan karbon, 1-D nanotuib karbon dan 2-D filem nipis grafen dalam kajian ini telah ditentukan dengan nilai 0.0148, 0.0109 dan 0.0045 kPa^{-1} dengan faktor tolok masing masing adalah 186, 136 dan 32, di mana melebihi penemuan yang telah dilaporkan sebelum ini. Keputusan juga menunjukkan bahawa peranti tekanan yang digabungkan dengan konfigurasi 0-D adalah lebih peka dalam tidak balas pada tekanan berbanding dengan konfigurasi 1-D atau 2-D, menunjukkan kesan piezo rintangan yang ketara dalam dimensi yang rendah. Keputusan yang cemerlang ini membuktikan bahawa bahan-bahan dimensi rendah berasaskan karbon yang digunakan dalam kajian ini menyediakan platform awal untuk potensi penyelidikan yang seterusnya bagi mencapai sasaran ultra-sensitif peranti takanan piezo rintangan.

LOW DIMENSIONAL CARBON BASED MATERIALS FOR LOW PRESSURE MEASUREMENT APPLICATION

ABSTRACT

Advances in materials science and engineering design have enabled the realization of flexible and highly sensitive pressure sensors. To date, numerous progresses on the invention of the piezoresistive pressure sensors based on the functional nanomaterials and the diaphragm structure have been widely demonstrated, in which great attention has been centered on improvement of sensitivity by the utilization of the functional nanomaterials and the optimization of the device geometries. However, real-time detection in low pressure range (<10 kPa) with excellent sensitivity has been rarely reported by the current progress of piezoresistive pressure sensors due to two apparent reasons: (i) lack of exploitation of functional nanomaterials through a controllable synthesis method and (ii) implementation of conventional diaphragm design structure. In view of that, this dissertation is intended to develop the flexible piezoresistive pressure sensor, which mainly focuses on the sensitivity enhancement with the incorporation of newly developed low dimensional carbon based materials and diaphragm structure with IDE array to satisfy the requirement of low pressure application. The novel features of low dimensional carbon based materials for 0-D carbon-capped nanoparticles, 1-D carbon nanotubes and 2-D graphene ultra-thin films have been introduced through chemical vapor deposition (CVD) and their morphology and electrical properties have been carefully characterized. Prior to the device fabrication, analyses on the characteristics of the reinforced diaphragm structure with interdigitated electrode (IDE) array have been accomplished through the CoventorWare® utilizing the finite element analysis (FEA). Parametric studies have been performed for all the simulations to evaluate the influence of geometrical parameters on the associated characteristics of interest. Two critical steps involved in the development of pressure sensor such as integration of IDE array on flexible substrate and transfer-printing method of low dimensional carbon based materials

have also been demonstrated. From the characterization results of low dimensional carbon based materials, uniformity and tunable morphology of the synthesized materials at different 0-D, 1-D and 2-D configuration in a control manner was achieved with excellent electrical properties. The technical findings highlighted in this study include the successful demonstration of novel features with mechanism model of carbon-capping in 0-D nanoparticles, horizontal growth formation in 1-D carbon nanotubes and defects enhancement in 2-D graphene films by CVD method. For the electromechanical characterization, it has been demonstrated that the fabricated flexible pressure sensor incorporated with low dimensional carbon based materials can be operated effectively at applied pressure below 10 kPa with high sensitivity, high linearity and high gauge factor in a response to small changes in pressure. The sensitivity of the fabricated sensors with 0-D carbon-capped nanoparticles, 1-D carbon nanotubes and 2-D graphene ultra-thin films in this research was determined to be 0.0148, 0.0109 and 0.0045 kPa^{-1} with gauge factor of 186, 136 and 32, respectively, in which outperformed the previous findings reported from the literatures. The results also demonstrated that the pressure sensor incorporated with 0-D configuration is more sensitive in a response to applied pressure than 1-D or 2-D configuration, suggesting a significant piezoresistive effect in the reduced dimension. This outstanding result proved that the low dimensional carbon based materials utilized in this present study provide the initial platform for further potential research to achieve the target of ultra-sensitive piezoresistive pressure sensor.

CHAPTER 1

INTRODUCTION

1.0 Background of piezoresistive pressure sensors

Pressure, defined as an expression of force exerted on a surface per unit area, is universal in basic operations in nature and human society. The SI unit for pressure is Pascal (Pa) and 1 Pa equivalents to a force of one Newton per square meter ($1\ Pa = 1\ N/m^2$) (Harvey, 1974). In many applications, it is necessary to know the working pressure that is usually generated by the contribution of the Earth's gravity, physical contact, and regular human and physiological activities. A pressure sensor is a device which is used to measure a specific pressure measurand, where the measurand is defined to be the physical quantity, property, or condition that is to be measured (Norton, 1982). Since the emerging area of MEMS and NEMS, hundreds of electronic devices with incorporation of nanomaterials have been constructed for specific applications such as transportation, aerospace, environmental monitoring, medical and healthcare, and a wide range of consumer products.

To date, numerous progresses on the invention of the piezoresistive pressure sensors such as diaphragm and piezoresistive sensing nanomaterials have been extensively studied by researchers, which offer a novel potential opportunity to improve the sensing capabilities in terms of sensitivity and linearity. The sensitivity is defined as $S = \Delta X/\Delta P$, where S is the sensitivity, X and P denote the quantitative output signal and applied pressure, respectively. Meanwhile, linearity is typically defined as the degree to which the actual performance of a sensor across a specified operating scale approximates a straight line. The rapidly advanced diaphragm material from silicon to organic polymers have contributed to significant progress of piezoresistive pressure sensors, which possess excellent properties such as high flexibility, simple fabrication process, low cost, and high sensitivity (Lee and Choi, 2008; Su et al., 2012; Gau et al., 2009; Hasenkamp et al., 2012). However, the utilization of the polymeric materials as flexible diaphragm structure needs to be incorporated with functional nanomaterials to further enhance the sensitivity of the piezoresistive pressure sensors for low pressure regimes. In particular, the current trend of piezoresistive pressure sensors involves the incorporation of metal nanoparticles, carbon nanotubes, silicon nanowires or graphene films as functional piezoresistive components onto the sensor platform, which can surpass the state-of-the-art silicon due to their excellent mechanical and electronic properties (Bsoul et al., 2011; Singh et al., 2013; Yao et al., 2013; Segev-Bar et al., 2013; Wong et al., 2014). Besides, the physical and electronic properties of these nanomaterials that can be altered through the synthesis process can also possibly open up new pathway to construct novel piezoresistive pressure sensors in order to satisfy the requirement of low pressure applications.

After years of extensive development of piezoresistive pressure sensors, significant achievements have been demonstrated in the evolution of functional piezoresistive materials from bulk to nanoscale technology, low-cost fabrication of pressure sensor with high sensitivity by the realization of polymer over silicon, and construction of integrated circuit towards practical applications. However, optimization on various parameters associated with the design, material selection, and device fabrication and network integrations still remains a main challenge before implementation of flexible pressure sensors in practical applications such as electronic skins (e-skins), human machine interactions and intelligent robotics, which greatly inspire the advancement of artificial intelligence systems.

1.1 Classification of pressure sensors

Pressure sensors are generally classified in terms of pressure regimes which cover a range spanning in ultra-low-pressure (<1 Pa), subtle-pressure (1 Pa to 1 kPa), low-pressure (1 to 10 kPa), medium-pressure (10 to 100 kPa) and high-pressure (>100 kPa) regimes. These specifics pressure distributions with their relevant sensing devices are shown in Figure 1.1. The ultra-low-pressure regime that refers to the pressure range below 1 Pa rarely occurs in daily basic activities. However, it is still worth noting that acoustic pressure or sound pressure, which is barely perceived by typical pressure sensors, is an example of pressure in this regime. The awareness of ultra-low pressure regimes has led to significant contributions in the development of ultra-sensitive microphones, hearing aids, hydrophones and other intelligent devices (Graz et al., 2006). The subtle-pressure regime (1 Pa to 1 kPa) is defined as pressure created by weak interactions of small objects. A sensitive response to such subtle-pressures is necessary for the construction of ultra-sensitive skin-inspired electronic devices that mimic the properties of human skin for potential applications in advanced robotics, prosthetics, and health monitoring technologies (Chortos and Bao, 2014).

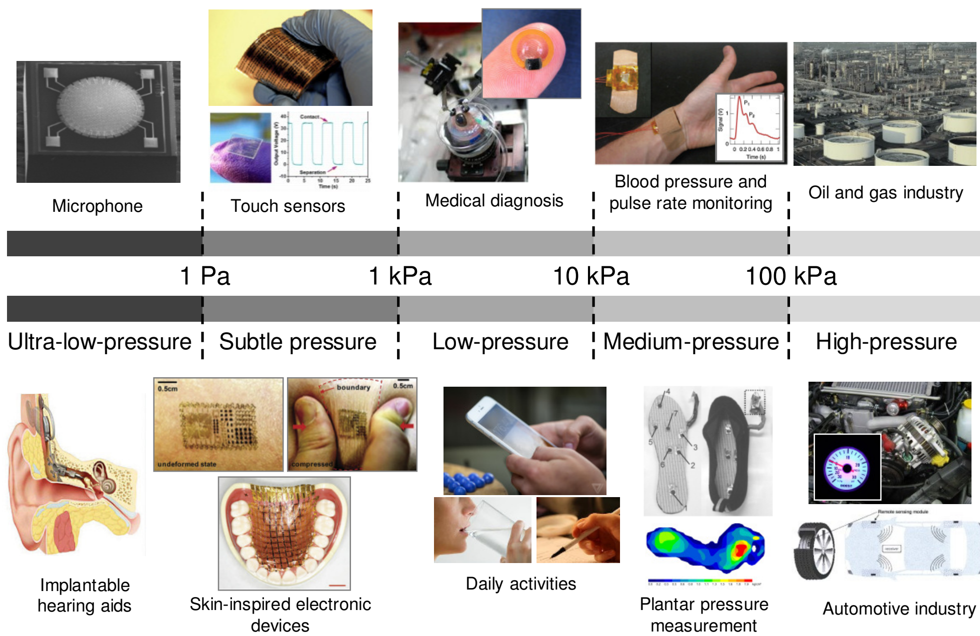

Figure 1.1 The schematic diaphragm of pressure regimes and the respective applications (Je et al., 2013; Pang et al., 2012; Zhu et al., 2014; Kim et al., 2011; Kaltenbrunner et al., 2013; Schwartz et al., 2013; Saito et al., 2011; and Munteanue et al., 2009)

The low-pressure regime covers a pressure range between 1 to 10 kPa, which is commonly existed in intra-body pressures and object manipulation on daily human activities. Many progresses have been initiated recently to construct highly-sensitive pressure sensors for applications for healthcare monitoring and medical diagnosis systems (Sekitani et al., 2010; Li et al., 2010; and Dagdeviren et al., 2014). For medium-pressure regimes (10 to 100 kPa), many types of sensors that are sensitive in this range have been widely developed for static pressure assessments, including plantar pressure between the foot and a supporting surface and pressure at high altitudes. In addition, the typical pressures by human body circulation are also distributed in medium-pressure regimes. The motivations to create a sensitive response to this pressure range have led to the innovative development of portable devices such as wearable electronic blood pressure sensor and pulse monitor devices (Li and Wang, 2011; Schwartz et al., 2013; and Choong et al., 2014). The assessment of high-pressure regime (>100 kPa) is very critical for automotive industry such as fuel injection, engine oil, transmission, turbo boost, tire-pressure monitoring and brake systems. In light of recent MEMS technology, sensors that are sensitive in this extreme pressure range are receiving much considerable attentions in order to meet their requirements with a simple, cost-effectiveness, reliable and robust concept (Eddy and Sparks, 1998 and Fleming et al., 2001). In the present study, the target range of pressure considered for the development of piezoresistive pressure sensor is 0 to 10 kPa.

1.2 Need for low dimensional materials as functional sensing components

Progress in advance materials of such low dimensional materials has gained great interest in the development of nanosensors due to relatively high surface-to-volume ratios and quantum confinement effects, leading to unique electronic, electromechanical and chemical properties in comparison to their bulk counterparts. A low dimensional material is defined as solid state materials with reduced dimension in one, two, or three directions. The low dimensional materials are generally classified as zero-dimensional (0-D), one-dimensional (1-D) and two-dimensional (2-D) configuration, which are illustrated in Figure 1.2. These materials can have ultra-high surface area to volume ratios where the surface states become dominant towards high selectivity, efficiency and rate of chemical reactions, thus offering high potential to create novel nanosensors with reduced power consumption, enhanced sensitivity and ultrafast response time.

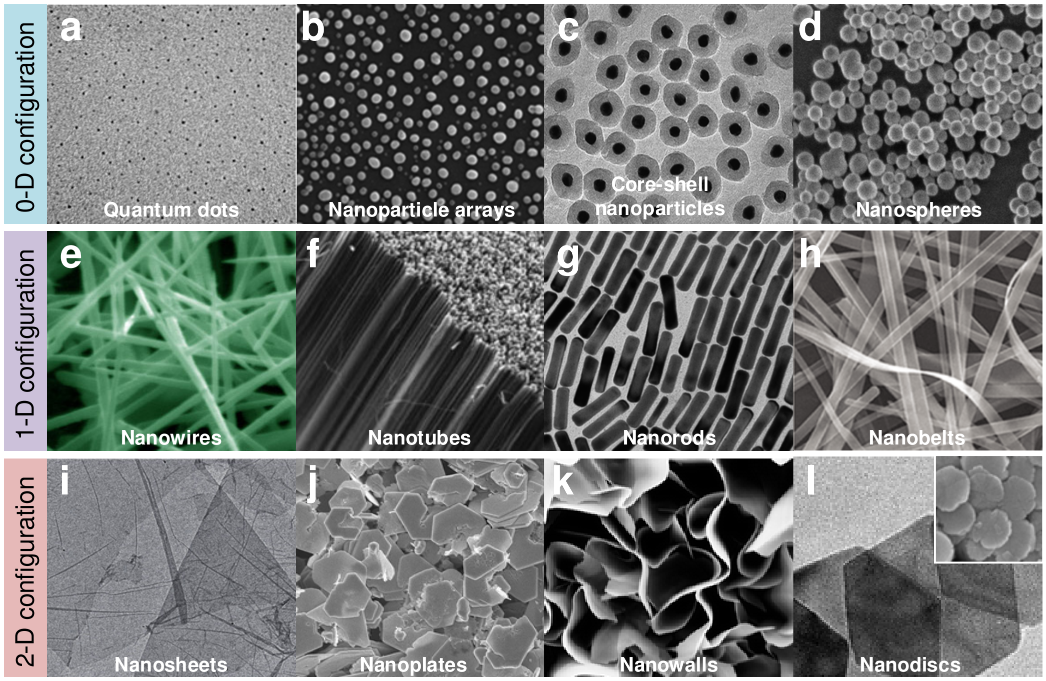

Figure 1.2 Typical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of low dimensional materials: (a-d) 0-D configuration (Pan et al., 2010; Zhao et al., 2014; Pazos-Pérez et al., 2010; and Medforth et al., 2009), (e-h) 1-D configuration (Cao et al., 2007; Miller et al., 2012; Bao et al., 2011; and Li et al., 2013) and (i-l) 2-D configuration (Li et al., 2012; Cheng et al., 2010; Gautam et al., 2005; and Mou et al., 2012)

In the bulk system, the conduction of electron is fully delocalized, in which the electrons can move freely in all dimensions. The electron transports are primarily determined by scattering with various mechanisms such as phonons, impurities, interfaces or other carriers. However, as the bulk system is reduced to the nanoscale with physical dimensional constraint, it gives rise to quantum confinement effects, which can significantly reduce the number of energy states available for electron conduction and the electrons become trapped along the reduced dimension (Ashby et al., 2009). In this case, the dependence of tunneling resistance and contact resistance on the strain state of the materials becomes dominant and more sensitive in response to mechanical input. Tunneling resistance is a resistance occurs by a tunneling mechanism when there is a gap or barrier between the nanomaterials, whereas a resistance between the nanomaterials that are physically in contact to allow the electron transport is known as contact resistance. The sensors that are based on networks of low dimensional materials have the benefit of incorporating nanoscale active sensing components with small volume, offering ultra-low power consumption, and increasing functionality of the devices. Furthermore, they also allow sensor miniaturization and create the possibility of expenditure in new applications such as skin-inspired electronic devices, gas sensors and electrochemical sensors (Sekitani and Someya, 2010; Liu et al., 2014; Lee et al., 2014).

1.3 Need for flexible substrate as functional diaphragm structure

Most of the development of micropressure sensors relies on the MEMS fabrication which has been done on a rigid silicon substrate using typical micromachining process such as bulk micromachining and surface micromachining (Madou, 1997). However, the silicon substrate used for micromachined sensors presents fundamental limitations. The fabricated sensor devices on rigid silicon substrate have significant drawbacks due to mechanical issues associated with it such as non-conformality on curvature surfaces and fracture due to its brittleness at thin structure (Engel et al., 2003). Presently there have been numerous interests in the realization of large-scale integration of MEMS sensors on flexible substrate due to their promising applications such as electronic skin, intelligent robotics, human-machine interactions, and biomimetic prosthesis, which greatly promote the innovation of artificial intelligence systems (Sekitani et al., 2010; Schwartz et al., 2013; Wang et al., 2013; Wang et al., 2014; and Zhang et al., 2014). The advantages of the flexible substrate to be used in integrated network sensors include (1) excellent mechanical strength; (2) high electrochemical stability; (3) high flexibility; (4) good electrical insulating; (5) lightweight and (6) cost-effectiveness.

There are three typical flexible substrates that have been utilized in the device fabrication process such as thinned glass (Auch et al., 2002 and Pinet et al., 2007), metal foil (Cheon et al., 2008 and Lee et al., 2011) and polymer (Engel et al., 2003). Flexible thinned glass substrates are ideally well-suited as a functional diaphragm for the development of ultra-sensitive optical based micropressure sensors due to their viable optical properties, but the drawbacks of thinned glass substrate are very difficult to handle due to their fragility. Metal foil substrates also exhibit high flexibility, thermal and mechanical durability, but they are conductive and have high surface roughness, thus require additional insulating coatings as well as surface polishing. Due to these restrictions, polymer substrates that are very flexible and cost-effectiveness have been widely fabricated, in which tend to be ideal candidates as functional diaphragm of micropressure sensors. In addition, their low elastic modulus also allows high deformation in response to small pressure and hence leads to high sensitivity.

1.4 Problem statement

There has been an increasing interest in research and development on miniaturized, ultra-sensitive, ultra-low power, instant-response, real-time monitoring, portable and robust sensors recently for industrial applications. Piezoresistive pressure sensor is one of the most successful sensor devices that benefits from the advancement of MEMS and NEMS technology. After rapid development of pressure sensors in the past few years, tremendous progress in the material science and engineering has been made which allows the incorporation of low dimensional materials onto the pressure sensors for enhanced sensing performance (Park et al., 2006; Bsoul et al., 2011; Zhu et al., 2013; and Smith et al., 2013). The rapid emerging in scaling down the sensing materials from bulk to nanoscale technology have contributed to numerous novel piezoresistive pressure sensors due to their excellent sensitivity and cost-effectiveness, thereby offering great potential for the realization of skin inspired electronic devices (Sekitani and Someya, 2010).

Despite the progress described above, many challenges still lie ahead before implementation of pressure sensors in practical low pressure applications. Based on the current development of piezoresistive pressure sensors, great attention has been centered on improvement of sensitivity by the optimization of device geometries and the utilization of the functional nanomaterials. These fabricated piezoresistive pressure sensors can also even surpass the-state-of-the-art silicon pressure sensor. Although many piezoresistive pressure sensors incorporated with low dimensional materials have been previously demonstrated, detection of low pressure regimes (<10 kPa) with excellent sensing capabilities has been rarely reported (Stampfer et al., 2006; Lou et al., 2012; and Zhu et al., 2013). Besides, the sensitivity of the piezoresistive pressure sensors is also insufficient and it requires further improvement of the functional nanomaterials in order to satisfy this target pressure range. In this case, it can be achieved by realizing the concept of piezoresistive effect which is principally, determined by the nature of material itself. Therefore, a better understanding of the fundamental sensing mechanism and exploitation of a novel sensing mechanism based on the functional low dimensional materials need to be taken into consideration to guide the construction of highly sensitive piezoresistive pressure sensors. Most of newly developed piezoresistive pressure sensors mainly rely on commercially available functional sensing materials (e.g. metal nanoparticles, carbon nanotubes, and graphene films) for the purpose of sensitivity enhancement (Cullinan and Culpepper, 2010; Zhu et al., 2013; Smith et al., 2013; and Wong et al., 2014). However, the utilization of these materials does not allow further alteration on the material itself and exhibit low piezoresistive effect, thereby limiting the sensing capabilities. Besides, the uniformity of these materials is also difficult to be controlled since these materials are mostly prepared in the form of liquid solutions. In view of that, synthesis of functional materials with novel features in a control manner is necessary to be considered for the development of highly sensitive piezoresistive pressure sensors.

Apart from the developments mentioned, the utilization of the flexible polymeric materials as effective diaphragm structure has attracted great attention for the development of piezoresistive pressure sensor due to their cost-effectiveness, high flexibility and low elastic modulus (Lim et al., 2005 and Gau et al., 2010). The excellent properties of polymeric materials can able to solve the ineffectiveness deflection of the-state-of-the-art silicon diaphragm in response to small applied pressure, which degrade the sensing performance. However, there has always been always been a trade-off issue between sensitivity and linearity, in which a greater sensitivity usually generates lower linearity and subsequently leads to the inaccurate measurements. It has been demonstrated that pressure sensors made of polymeric materials can achieve high sensitivity, but they also exhibits high nonlinearity (Yao et al., 2014). In order to meet the requirements for particularly low pressure application, it is therefore necessary to develop a robust diaphragm structure for piezoresistive pressure sensor with excellent sensing capabilities.

In view of this, a piezoresistive pressure sensor incorporated with novel features of functional sensing materials and effective diaphragm structure, has to be constructed using controllable synthesis method of 0-D, 1-D, and 2-D low dimensional carbon based materials, which contributes to significant impact to the pressure sensing performance in order to address the current shortcoming.

1.5 Research objectives

The main objective in this research work is to develop a highly sensitive flexible pressure sensor by using low dimensional carbon based materials for low pressure application. In order to achieve this main objective, following sub-objectives need to be accomplished:

Objective 1 : To develop novel features of 0-D carbon-capped nanoparticles, 1-D carbon nanotubes and 2-D graphene ultra-thin films as functional sensing materials through a controllable synthesis method and systematic characterization

Objective 2 : To design and simulate reinforced diaphragm structure integrated with interdigitated electrode (IDE) arrays using commercially available FEA software for enhanced sensitivity and linearity

Objective 3 : To fabricate, test and characterize highly sensitive flexible piezoresistive pressure sensor incorporated with low dimensional carbon based materials for low pressure regimes (<10 kPa).

Objective 4 : To achieve high sensitivity and gauge factor from the effect of incorporation of low dimensional carbon based materials, which is comparable or higher than previous literatures

1.6 Thesis outline

The thesis is presented in six chapters which include introduction, literature review, methodology, systematic study on low dimensional carbon based materials, development of flexible pressure sensor with low dimensional carbon based materials, and finally conclusion. The second chapter emphasizes literature review regarding exploration of functional piezoresistive materials, synthesis of low dimensional materials, and development of functional diaphragm for micropressure sensors. This chapter also deals with the past and modern trends in the development of micropressure sensors incorporated with active sensing components from bulk to nanoscale technology and the fabrication technology of diaphragm from silicon to polymer. From this chapter, numerous ideas can be generated to modify the existing fundamental and conceptual of micropressure sensors or to create novel micropressure sensors based on the realization of present researches towards significant and original contribution of knowledge. In third chapter methodology of this research project that has been carried out for synthesis and characterization method of low dimensional carbon based materials such as 0-D carbon-capped nanoparticles, 1-D carbon nanotubes, and 2-D graphene ultra-thin films are described. In addition, this chapter describes the construction of pressure sensors with the associated FEA, fabrication and characterization in response to the applied pressure also are described accordingly. Test setup to evaluate the performance of the fabricated pressure sensor is also included in the same chapter. Chapter four presents and discusses the results obtained from synthesis and characterization of low dimensional carbon based materials that are utilized as active sensing components in the fabricated pressure sensors. In chapter five the results extracted from the FEA, fabrication and characterization involved for the fabricated pressure sensor incorporated with the low dimensional carbon based materials are presented and discussed accordingly. Finally, the thesis ends with conclusion and recommendations for future works in chapter six.

CHAPTER 2

LITERATURE REVIEW

2.0 Overview

This chapter presents the literature review on the background and prior published literatures related to various components of this present study. This review is not only serves to justify some of the development concepts in this research and to realize the issues or limitations related to the existing pressure sensors, but it also provides a new avenue for modifying the fundamental properties to improve the recent development of pressure sensor.

2.1 Exploration of functional piezoresistive materials for pressure sensor: From bulk to nanoscale technology

Majority of pressure sensors developed is piezoresistive pressure sensors, in which these sensors utilize the invention of bulk silicon, germanium or polysilicon as an active component to substitute the state-of-the-art of metal strain gauges in order to enhance the sensitivity of output signal (Barlian et al., 2009; Bhat and Nayak, 2013). However, the bulk technologies implemented in the existing pressure sensors are only suitable for large pressure application in the range of 0-1000 kPa, and it has limitation in the output response when measuring a small change of pressure for low pressure application because of lower sensitivity and resolution (Bao et al., 1989; Lin et al., 1998; Zhang et al., 2007 and Tiwari and Chandra, 2013). In order to overcome these issues, a novel nanoscale piezoresistive material that offers an enhanced piezoresistance effect with respect to the bulk counterparts is significantly crucial for developing highly sensitive pressure sensors.

The piezoresistive-based transduction mechanism is commonly utilized in the pressure sensors due to their simple device structure, easy read-out mechanism and potentially high pixel density (Pan et al., 2014). To develop novel functional sensing components with exceptional and comprehensive sensing capabilities, numerous significant aspects should be carefully considered, in which these aspects mostly rely on the classification and geometrical of sensing components (Barlian et al., 2009 and Zang et al., 2014). The development of the piezoresistive pressure sensor over the years highlighting on their respective piezoresistive effect in low-dimensional materials and the synthesis method of the piezoresistive components are reviewed in the following subsection.

2.1.1 Basic structure of piezoresistive pressure sensors

The typical piezoresistive pressure sensors that have been widely used to monitor the pressure changes can be illustrated in Figure 2.1. These sensors generally comprise of several basic components: (i) diaphragm that deflects when pressure exerts on it; (ii) sensing elements to convert the mechanical stress or strain to output signals and (iii) electrical contact for integrated external circuit (Bhat and Nayak, 2013; Kumar and Pant; 2014). The working principle of miniaturized pressure sensors are based on the uniform pressure applied on the one side of the diaphragm, which consequently leads to the deformation of the diaphragm to generate an output signal.

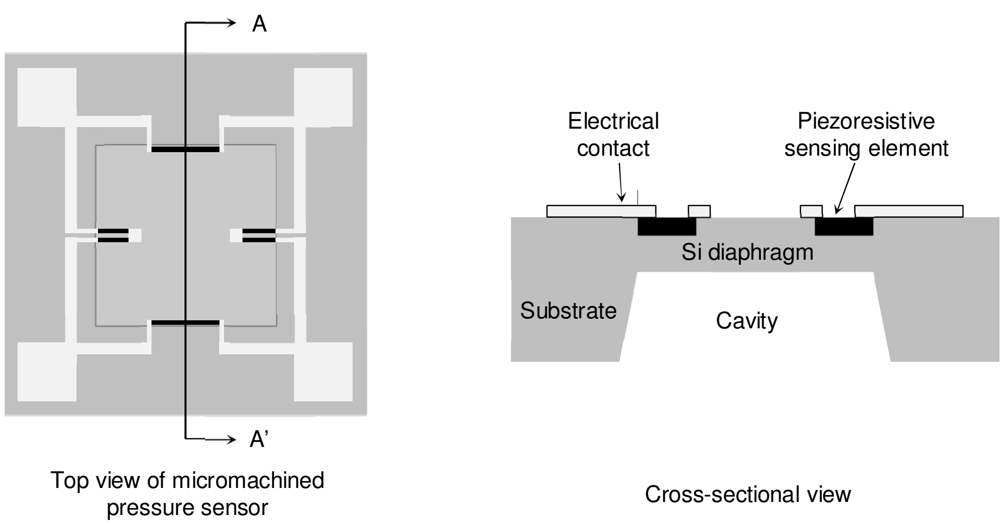

Figure 2.1 Illustration of a typical diaphragm based micromachined piezoresistive pressure sensor with piezoresistors as sensing element

2.1.2 Recent progress of piezoresistive pressure sensors

Several studies related to the piezoresistive pressure sensors and their modifications have been extensively reported with low nonlinearity while retaining the sensitivity. It was demonstrated that the sensitivity and linearity of the piezoresistive pressure sensors can be achieved by modifying either the piezoresistor arrangement or the diaphragm structure (Pancewicz et al., 1999; Aravamudhan and Bhansali, 2008; and Tian et al., 2012). In addition, the inventive design of '*n*'-shaped, meander-shaped or '*x*'-shaped piezoresistors as effective sensing element have been also introduced onto the diaphragm in order to enhance the sensitivity and linearity of the sensors (Motorola Inc, 1998; Bae et al., 2004; Wu et al., 2006; and Zhang et al., 2007). However, the use of silicon as diaphragm and piezoresistors in these sensors was applicable for high pressure measurements due to high rigidity of substrate and low sensitivity, thereby limiting their resolution at low pressure range. Furthermore, the silicon piezoresistive pressure sensors are also highly temperature-dependent; thereby requiring an additional Wheatstone bridge configuration to compensate the change in resistance of piezoresistors caused by the temperature coefficient of resistance (TCR) (Kumar et al., 2014). From the previous literatures, the sensitivities of silicon based piezoresistive pressure sensors were reported, ranging from 1.0×10^{-5} to 3.5×10^{-3} kPa^{-1} (see Table 2.1).

Due to these drawbacks of existing piezoresistive pressure sensors, several progresses on the size-reduction of piezoresistors, from bulk silicon towards 1-D silicon nanowires (SiNW) have attracted much attention for the advance development of the piezoresistive sensors. The novel approach of this type of piezoresistive pressure sensor is the substitution of the Si piezoresistors with the 1-D SiNW. The 1-D SiNW also can play the same role as highly doped bulk silicon in the typical pressure sensors. The concept of using 1-D SiNW as piezoresistors was firstly proposed by Toriyama et al. (2002), in which the piezoresistance effect increases with a decrease in the cross-sectional area of the SiNW. After realizing the giant piezoresistance effect in SiNW, Lou et al. (2012) introduced an ultrasensitive SiNW based piezoresistive pressure sensor with sensitivity of 4.6×10^{-3} kPa^{-1}, which was comparable to other recently reported piezoresistive pressure sensor due to the issues of thick diaphragm. Further modification of diaphragm with thinner annular grooved structure by Zhang et al. (2014) improved the device sensitivity by 2.5 times higher than the sensitivity reported by Lou et al. (2012). The SiNW embedded with groove and rib structures are illustrated in Figure 2.2(a) and (b). However, the grooves and ribs structure on the diaphragm result in very complex fabrication process, which requires additional front side etching process.

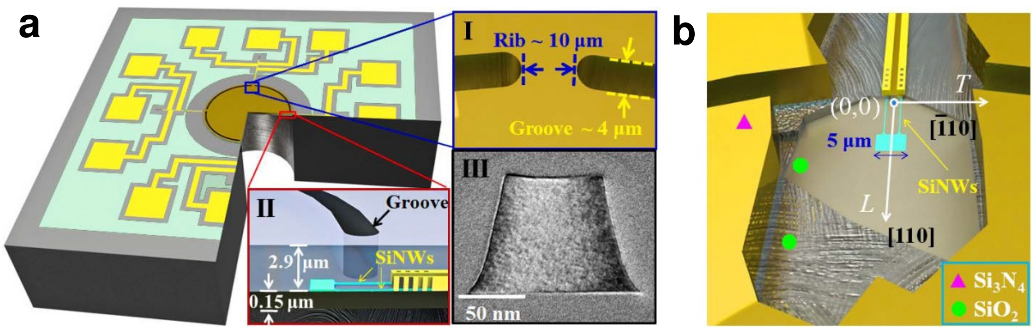

Figure 2.2 (a) The schematic of 1-D SiNW embedded with groove and rib structures on the circular diaphragm (released from the back side) and (b) the spot view of 1-D SiNW patterned along [110] direction after etching back top passivation layers (2.5 µm Si_3N_4 and 0.4 µm SiO_2). Inset I: the close-up view of the micro-groove; inset II: the cross-sectional view of the multilayer diaphragm and inset III: a TEM image for the cross-sectional of the nanowire (Zhang et al., 2014)

Despite of the drawbacks of silicon based piezoresistors, several advancements on the low-dimensional carbon based materials such as 1-D carbon nanotubes (CNT) and 2-D graphene as piezoresistive components on silicon diaphragm have been widely investigated with considerable potential for future high-sensitivity low power devices. For 1-D CNT, Liu and Dai (2002) demonstrated that the piezoresistive pressure sensors can be realized using the concept of piezoresistance effect in single-walled carbon nanotubes (SWCNT), which was firstly proposed by Tombler et al. (2000). The SWCNT was grown on suspended square polysilicon membranes as shown in Figure 2.3(a). A reversible resistance change in the SWCNT was observed when uniform air pressure was applied and pumped out on the membranes, indicating the robustness of the SWCNT. Later, Stampfer et al. (2006), Cullinan and Culpepper (2010) and Burg et al. (2011) further reported on the fabrication and characterization of piezoresistive pressure sensors based on individual SWCNT as the active piezoresistive components, which adhered directly on the membrane (see Figure 2.3(b-d)). Meanwhile, the similar concept to this also was utilized by Park et al. (2006) to develop a piezoresistive pressure sensor with a single carbon fiber attached between two electrodes (see Figure 2.3(**e**)).

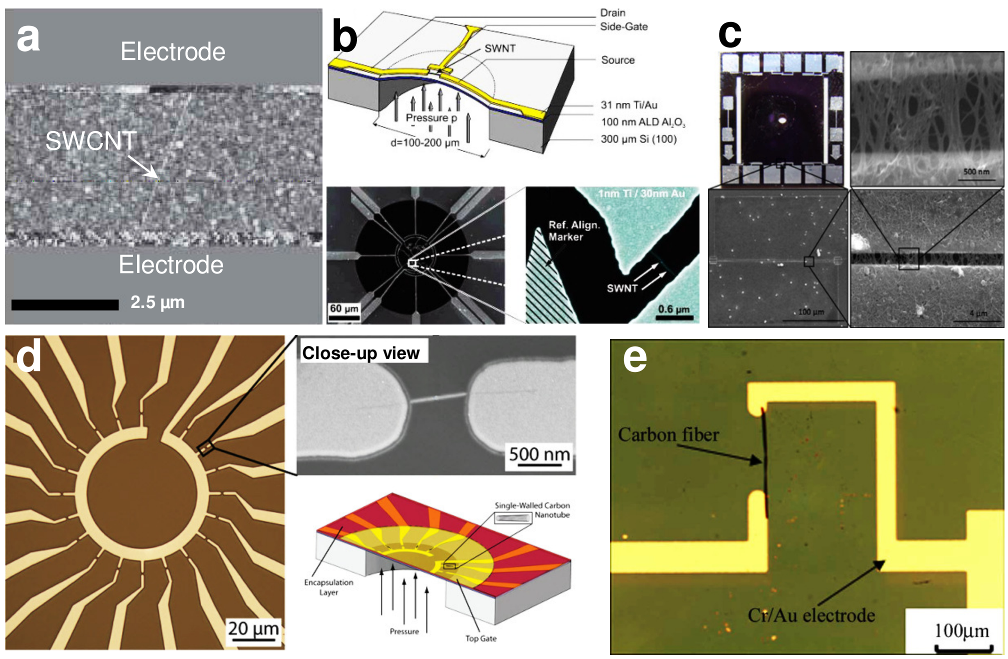

Figure 2.3 (a) AFM image of a SWCNT connection between two metal electrodes (Liu and Dai, 2002). (b) Schematic of the SWCNT based pressure sensor. The inset shows SEM images of a device consisting of an alumina membrane with electrically contacted SWCNT (Stampfer et al., 2006). (c) SEM images of SWCNT resistor network between two electrodes on the test structure (Cullinan and Culpepper, 2010). (d) Optical image of circularly arrangement electrodes with dielectrophoresis SWCNT integration. The inset shows the SEM image of a bridged electrode gap with a good SWCNT alignment (Burg et al. 2011). (e) Optical image of carbon fiber assembled between two electrodes (Park et al., 2006)

Although the incorporation of SWCNT or carbon fiber onto silicon membrane exhibits much higher sensitivity compared to the state-of-the-art silicon piezoresistors, there still remains numerous challenges to fabricate commercially viable individual SWCNT or carbon fiber based pressure sensors. One of the main challenges is to control precise nanotube positioning by using direct assembly by dielectrophoresis. Based on the previous process by Burg et al. (2011), the SWCNT or carbon fibers have to be individually dispersed in solution and a drop of the solution needs to be applied on the gap between the electrodes in a controlled manner where the biased AC electric field is applied. It is also very difficult to control the process due to the random agglomeration of SWCNT or carbon fibers into solvents, thus circumventing the formation of individual SWCNT or carbon fiber.

In order to simplify the fabrication process of the piezoresistive pressure sensors, Bsoul et al. (2011) introduced the piezoresistive pressure sensor with direct growth of vertically aligned multi-walled carbon nanotubes (MWCNT) films on the membrane using CVD technique as illustrated in Figure 2.4(a). It was demonstrated that the MWCNT films also exhibit piezoresistivity with an applied of lateral stress. However, the sensitivities reported for the MWCNT based piezoresistive pressure sensors is slightly lower in comparison to those of SWCNT based piezoresistive pressure sensors due to ineffective resistance changes under deformation as a result of highly-dense formation of MWCNT films. In order to solve this problem, Lim et al. (2011) introduced a novel wavy structured substrate incorporated with carbon-nanotube thin film (CNTF) as shown in Figure 2.4(b) to further enhance the pressure sensitivity. By controlling the surface structures of the substrate, it is possible to tune the pressure sensitivity of the CNTF/PDMS hybrid. Such structure also improves the mechanical stability of the device, thereby resulting in robust sensing operations. Besides, the use of sandwitched-like structure of polydimethylsiloxane (PDMS), carbon microcoils (CMC) and carbon nanofiber (CNF) for the purpose of enhancing the pressure sensitivity was reported by Su et al. (2012). The CMC/CNF structure as an active piezoresistive component is illustrated in Figure 2.4(c). It should be noted that although the sensitivity of CMC based pressure sensor increases with increasing the yield of CMC, the consistency of output response was very poor due to large variations of resistance. Singh et al. (2013) reported that the sensitivity of MWCNT-polyimide nanocomposite based piezoresistive pressure sensor increases with reducing concentration of MWCNT from 10%

to 1%, but higher operating voltage is required due to small current. Besides, the orientation and alignment of MWCNT in the polyimide are difficult to control, hence may introduce inconsistent results. Therefore, there still needs several improvements of the piezoresistive components in order to achieve high reliability and robustness of the output response.

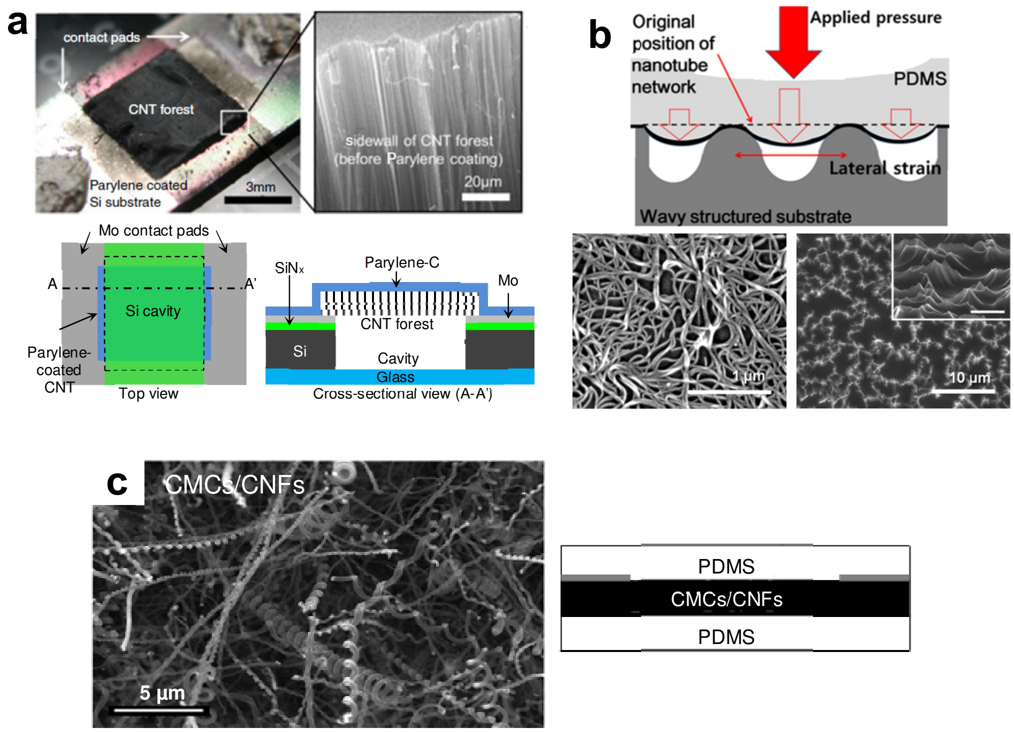

Figure 2.4 (a) Fabricated piezoresistive pressure sensor with vertically aligned MWCNT forest. SEM image shows the high-density of as-grown MWCNT (Bsoul et al. 2011). (b) Schematic of a cross-sectional view of the CNTF/PDMS hybrid on a way structured substrate. SEM images of the CNTF transferred to the PDMS surface and the wavy structured Si substrate (Lim et al., 2011). (c) SEM image of CMC/CNF structures as piezoresistive component in between sandwitched-like structure of PDMS (Su et al., 2012)

Recently, the use of 2-D graphene onto the piezoresistive pressure sensors is considered as novel sensing nanomaterial since its discovery in 2004 by Novoselov et al. (2004). The first graphene based piezoresistive pressure sensor using monolithic integration in silicon based on standard semiconductor processes was developed by Zhu et al. (2013). They demonstrated the multilayer graphene meander patterns located on the maximum strain area of silicon nitride (SiN_x) suspended membrane, in which it was invented using highly-cost electron-beam lithography as illustrated in Figure 2.5(a). However, the sensing performance of the fabricated sensor is not remarkable due to the utilization of commercial pristine multilayer graphene film, which has low gauge factor of ~1.6. Instead of using silicon based membrane as a structural element or multilayer graphene films as a sensing element in the pressure sensors, Smith et al. (2013) introduced the electromechanical piezoresistive sensing in suspended graphene, which fully utilized the monolayer graphene as effective piezoresistive components and membrane as shown in Figure 2.5(b). The cavities were fabricated using reactive ion etching (RIE) to provide vertical etch profiles, thus allowing the gas pressure to be directly applied on the suspended graphene membrane.

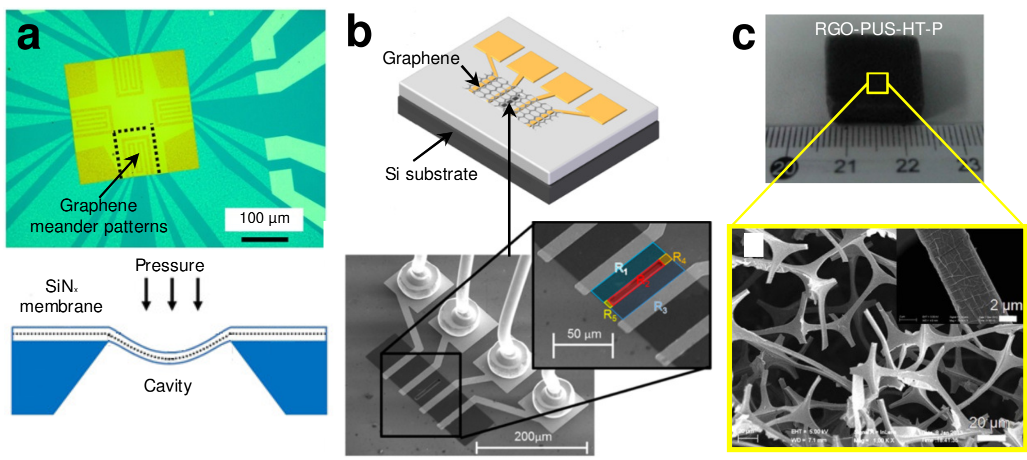

Figure 2.5 (a) Optical image of graphene meander patterns piezoresistors on silicon nitride square membrane and schematic of the suspended membrane under the applied pressure (Zhu et al., 2013). (b) Schematic of graphene based pressure sensor and SEM images of suspended graphene as membrane and piezoresistive component (Smith et al., 2013). (c) Photograph of the compressed RGO-PU-HT sponge and the corresponding SEM image of fractured microstructures (Yao et al., 2013)

Although the graphene membrane is the most robust material known, it was demonstrated that the graphene based piezoresistive pressure sensors was only able to achieve sensitivity of 3.0×10^{-5} kPa^{-1}, which is almost lower than those of silicon or CNT based piezoresistive pressure sensor. The same result to this was also observed in the graphene based piezoresistive pressure sensor by Zhu et al. (2013) due to small deflection of the SiN_x membrane, which in turns limits the piezoresistive effect of graphene. In order to solve these limitations, Yao et al. (2013) proposed the large-scale flexible pressure sensor with hydrothermally and compressed treated reduced graphene oxide-polyurethane (RGO-PU-HT-P) sponge based on novel fractured microstructure design (see Figure 2.5(c)). The high sensitivity of the sensor from 0.03 to 0.26 kPa^{-1} at pressure range of 0-10 kPa can be achieved. However, the sensor exhibits nonlinear output response in this pressure range, thus restricted its sensing capabilities for low pressure applications.

Incorporation of monolayer-capped nanoparticles onto arbitrary substrates can also offer a new generation of highly sensitive pressure sensors that could meet specification of low pressure applications. Segev-Bar et al. (2013) presented the flexible pressure sensors based on monolayer-capped nanoparticles (MCNP) as shown in Figure 2.6, where the fabricated sensors were made of Au nanoparticles with 3-ethoxythiophenol as capping ligand (ETP-MCNP) on various flexible substrates. It was demonstrated that the sensitivity of the fabricated sensors mainly depended on the substrate properties, thereby allowing modulation of sensitivity using the same ETC-MCNP layers. However, the incorporation of ETC-MCNP by drop-casting method was inconsistent, thus leading to possible particle agglomeration. Apart from that, the sensitivity enhancement of the sensors is not only limited to the types of substrate used, but may also depend on the arrangement of MCNP layers, which considers the different composition metal nanoparticles, densities and gaps. Furthermore, the effects of these variables on the pressure sensitivity have not yet been reported for the piezoresistive pressure sensor.

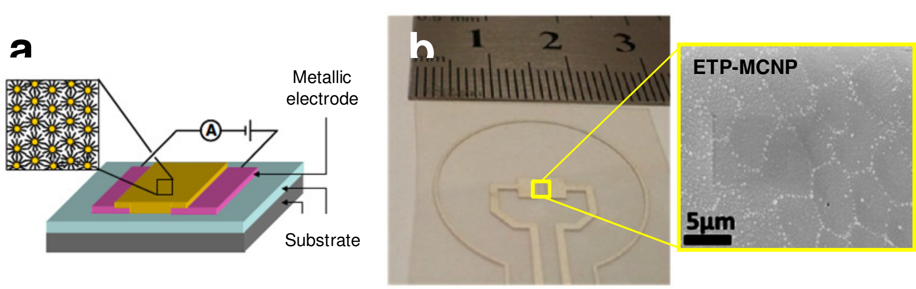

Figure 2.6 (a) Schematic of flexible pressure sensor based on ETP-MCNP layers. (b) Photograph of actual device on flexible substrate. The inset shows the SEM image of ETP-MCNP drop-casted layer on flexible substrate (Segev-Bar et al., 2013)

From the discussion presented, there are many ways to enhance the pressure sensing performance of piezoresistive pressure sensors as proposed in the published literatures. Table 2.1 summarizes the recent progress of piezoresistive pressure sensors with known working pressure range, sensitivity, and their corresponding piezoresistive components and aspects of novelty. It should be noted that the Si doped piezoresistors have been widely engaged as integration parts in piezoresistive pressure sensors based on compatible process of integrated circuit (IC) technology. The Si based pressure sensors also have a leading sensitivity over metallic based pressure sensors (strain gauges) for past decades until the emerging of low dimensional materials as the piezoresistive components such as SiNW, CNT, graphene, and metallic nanoparticles. Although such kind of nanomaterials possess excellent electromechanical properties in response to the pressure, there is still a room of improvement that should be identified in order to further improve the sensing capabilities of the existing piezoresistive pressure sensors at a specific pressure regime. Moreover, the incorporation of these nanomaterials onto different sensor platforms also gives the variation of sensitivity. The comparison of sensitivity between these sensing nanomaterials has also not yet been reported. In view of that, piezoresistive pressure sensors incorporated with low dimensional carbon based materials such as 0-D carbon-capped nanoparticles, 1-D carbon nanotubes, and 2-D graphene are demonstrated in the present research. The novel structure of these materials onto flexible substrate is introduced to achieve highly sensitive piezoresistive pressure sensors. The sensitivities reported from previous literatures are to be compared with the piezoresistive pressure sensors presented in this research, which are discussed in details in Chapter 5. Such comparison is important to define the degree of achievement of the fabricated pressure sensors.

Table 2.1 Summary of recent development of piezoresistive pressure sensors from previous published literatures

Author(s)	Aspects of novelty	Piezoresistive component	Type of membrane/ Young's Modulus, E	Pressure range/ Sensitivity	Gauge factor
Samaun et al. (1973)	Standard integrated-circuit (IC) processing technique.	p-doped Si	Si (100)/ 179 GPa	0 – 18.7 kPa/ 6.23×10^{-4} kPa^{-1}	n/a
Ko et al. (1979)	A resistive bridge diffused on a <100> oriented silicon wafer at the center of diaphragm.	p-doped Si	Si (100)/ 179 GPa	0 – 40 kPa/ 7.5×10^{-5} kPa^{-1}	n/a
Kim and Wise (1983)	A new technique of the electrochemical etch-stop for diaphragm formation.	p-doped Si	Si (100) / 179 GPa	0 – 107 kPa/ 9.98×10^{-5} kPa^{-1}	n/a
Sugiyama et al. (1991)	Micro-diaphragm pressure sensor structure with '*c*'-shaped cavity.	p-doped polysilicon	Si_3N_4 / 310 GPa	0 – 300 kPa/ 1×10^{-5} kPa^{-1}	n/a
Sandmaier and Kuhl (1993)	Novel diaphragm design of rectangular central boss.	p-doped Si	Si (100)/ 179 GPa	±10 kPa/ 3.5×10^{-3} kPa^{-1}	n/a
Wu et al. (2006)	Development of high-temperature pressure sensors based on 3C-SiC piezoresistors.	3C-SiC film	Poly-SiC/ 308 GPa	0 – 500 kPa/ 2.58×10^{-5} kPa^{-1}	2.1
Zhang et al. (2007)	Meander-shaped piezoresistors on silicon micro pressure sensor.	p-doped Si	Si (100)/ 179 GPa	0 – 1000 kPa/ 3.22×10^{-5} kPa^{-1}	n/a
Aravamudhan and Bhansali (2007)	Reinforced diaphragm structure with thin and thick structure.	p-doped Si	Si (100)/ 179 GPa	0 – 1380 kPa/ 1.07×10^{-4} kPa^{-1}	n/a
Tian et al. (2012)	Novel diaphragm design of cross-beam structure.	p-doped Si	Si (100)/ 179 GPa	0 – 5 kPa/ 1.55×10^{-3} kPa^{-1}	n/a
Lou et al. (2012)	Novel NEMS pressure sensors with a multilayered diaphragm using SiNW as piezoresistors.	SiNW	SiN_x/SiO_2 200 GPa/ 70 GPa	0 – 140 kPa/ 4.6×10^{-4} kPa^{-1}	78
Stampfer et al. (2006)	Development of individual SWCNT as piezoresistors at center of diaphragm.	SWCNT	Al_2O_3 / 189 ± 25 GPa	0 – 120 kPa/ 1.2×10^{-3} kPa^{-1}	210
Park et al. (2006)	Development of individual carbon fiber as piezoresistors at edges of diaphragm.	Carbon fiber	SiO_2/ Si (100)/ 70 GPa/ 179 GPa	0 – 100 kPa/ 6.0×10^{-4} kPa^{-1}	50

Table 2.1 (Cont.)

Lin et al. (2010)	Monolithic integration of carbon nanotubes pressure sensors.	MWCNT	Parylene-C/ 2.8 GPa	0 – 50 kPa/ 1.4×10^{-3} kPa^{-1}	20
Burg et al. (2011)	Parallel integration of individual SWCNT by dielectrophoresis (DEP).	SWCNT	Al_2O_3/ SiO_2 / 189 ± 25 GPa / 70 GPa	0 – 5 kPa/ 2.5×10^{-3} kPa^{-1}	n/a
Bsoul et al. (2011)	Vertically aligned carbon nanotubes forest supported by Parylene-C membrane.	MWCNT	Parylene-C/ 2.8 GPa	0 – 60 kPa/ 9.0×10^{-4} kPa^{-1}	n/a
Lim et al. (2011)	Novel wavy structured substrate.	CNTF	PDMS/ 0.75 GPa	0 – 30 kPa/ 5×10^{-3} kPa^{-1}	n/a
Su et al. (2012)	Development of carbon microcoils as piezoresistors.	Carbon microcoils	PDMS/ 0.75 GPa	0 – 14 kPa/ 9.3×10^{-3} kPa^{-1}	n/a
Singh et al. (2013)	Development of MWCNT-PI nanocomposite with different MWCNT concentrations.	MWCNT-PI	MWCNT-PI / 2.71 GPa	40 – 240 kPa/ 0.025 kPa^{-1}	n/a
Zhu et al. (2013)	Piezoresistive pressure sensor with graphene meander patterns piezoresistors using monolithic integration in silicon based MEMS.	Graphene	SiN_x / 200 GPa	0 – 70 kPa/ 3.4×10^{-5} kPa^{-1}	1.6
Smith et al. (2013)	Piezoresistive pressure sensor based on suspended graphene membranes with direct electrical signal readout.	Graphene	Graphene / 1 TPa	0 – 60 kPa/ 3.0×10^{-5} kPa^{-1}	2.92
Yao et al. (2013)	Fractured microstructure design.	Reduced-GO	PU/ 0.025 GPa	0 – 10 kPa/ 0.03 – 0.26 kPa^{-1}	n/a
Segev-Bar et al. (2013)	Nanoparticle based flexible pressure sensor using various substrates.	ETP-MCNP	Polyester/ 4.1 GPa	0 – 3 g/ 0.01 – 0.23 g^{-1}	250
Wong et al. (2014)	SU-8 micro pressure sensor fabricated using SU-8/silver nanocomposite.	SU-8/Silver nanocomposite	SU-8/ 2.0 GPa	0 – 10 kPa/ 2.15×10^{-3} kPa^{-1}	26.3

2.1.3 Piezoresistive effect

The piezoresistive effect describes the change in material's electrical resistivity due to applied mechanical pressure or strain. It was first discovered by Lord Kelvin who revealed the change in resistance with elongation in iron and copper, in which the effect observed strictly depends on variations in their resistivities since the elongation was the same for both wires (Thomson, 1856). For metal, it was noticed that the resistance change effect was dominated by the geometry change in material. The electrical resistance R of a physical material at steady state and under deformation can be described by the following equation:

$$R = \rho \frac{l}{A} = \rho \frac{l}{(w)(h)} \quad \text{(Steady state)} \tag{2.1}$$

$$R = \rho \frac{\Delta l + l}{(\Delta w + w)(\Delta h + h)} \quad \text{(Under deformation)} \tag{2.2}$$

where $\rho, l, A, w,$ and h is the resistivity, length, cross-section area, width and thickness of material.

It was discovered that semiconductors such as silicon and germanium exhibited a much greater piezoresistive effect than metals, thus generating significant interest in semiconductor stress-strain sensing devices (Smith, 1954). In single crystal silicon (Si) and germanium (Ge), two phenomena attributed to the changes in resistivity: the stress dependent distortion of its geometry and the stress dependence of its resistivity (Barden and Shockley, 1950; Smith, 1954; and Herring, 1956). For crystal Si, it has been reported that the piezoresistive effect is 50 to 100 more significant in comparison to geometry effect due to the presence of the wide energy band gap (~1.11 eV), in which the electronic properties can be tuned by the application of stress or strain (Kittel, 1986 and Barlian et al., 2009). The relative change in resistance of the representative semiconductor material as it is subjected to the applied stress or strain is given by the following equation (Kanda, 1991):

$$\frac{\Delta R}{R} = \frac{\Delta \rho}{\rho} + \frac{\Delta l}{l} - \frac{\Delta w}{w} - \frac{\Delta h}{h} \tag{2.3}$$

where $\Delta\rho$, Δl, Δw, and Δh are the changes in the respective parameters due to the applied stress or strain. The width (w) and the thickness (h) are the parameters of the cross-section area reduced in proportion to the longitudinal stress or strain along the length (l) by its Poisson's ratio (v), which can be expressed by

$$\frac{\Delta w}{w} = \frac{\Delta h}{h} = -v\frac{\Delta l}{l} \tag{2.4}$$

The gauge factor (g) is a key parameter to evaluate the sensitivity of piezoresistive material and equivalent to the ratio of relative change in resistance to strain. It is widely used to describe the performance of pressure sensors. Higher gauge factor improves the sensitivity of the sensor devices by generating higher resistance change under the identical loading, which can be expressed by the following equation (Bao, 2000 and Barlian et al., 2009):

$$g = \frac{\Delta R/R}{\varepsilon} = (1 + 2v) + \frac{\Delta\rho/\rho}{\varepsilon} \tag{2.5}$$

where ε is strain and $\Delta R/R$ is relative resistance change with strain. The change in resistance is due to both the geometrical effect $(1 + 2v)$ and the relative change in resistivity $(\Delta\rho/\rho)$ with strain.

It has been reported that the gauge factor of doped Si as piezoresistor in pressure sensor is ~50-170, which is about 1-2 orders of magnitude higher than that of metals (Toriyama and Sugiyama, 2002). Although the piezoresistive effect in Si contributes much value in developing piezoresistive pressure sensor, the output response only attributed to the change in the energy band gap and it is not suitable to be employed in a specific sensor device for low pressure detection due to its low sensitivity and limited resolution. In addition, the most widely used form of piezoresistive sensors are bulk diffused Si and polysilicon piezoresistor (Guckel et al., 1990; Toriyama and Sugiyama, 2002; Malhaire and Barbier et al., 2003; and Alpuim et al., 2008). However, the fabrication of these piezoresistive components can only be achieved by the use of Si or polysilicon substrate, thus limiting the selection of flexible substrate for low cost fabrication. Graphite as an