M.S. THESIS

Solution Processed CNT Device Analysis and Temperature Sensor Array Implementation

용액 공정 CNT 소자 분석 및 온도센서 어레이 응용에 관한 연구

BY

Farah T. Al-Naimi

AUGUST 2012

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이 논문을 공학석사 학위논문으로 제출함

2012 년 8 월

서울대학교 대학원

전기컴퓨터 공학부

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Farah T. Al-Naimi 의 공학석사 학위논문을 인준함

2012 년 8 월

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Abstract

As robotics and prosthetic limbs become more of a necessity than a luxury the so is the ability to enable them to feel. This results in more realistic responses from robotics and also enables owners of these prosthetic limbs to recover the senses that they lost, and thereby returning to a normal functioning lifestyle.

The sensors considered so far by many research groups interested in electronic skin (E-skin) have been pressure and temperature sensors, the latter of these is the one considered in this thesis. The temperature range considered in this thesis is (30 – 100)^{o}C and the temperature sensitive material used is one which has gained much interest over the past decade, namely, carbon nanotubes (CNT). Two types of ink were considered including one multiwalled CNT (MWNT) and one Singlewalled CNT (SWNT). The two inks were thoroughly examined and characterised in different environmental conditions to determine their suitability for the application mentioned above.

It was found that MWNT was the suitable candidate since it consistently gave the most linear resistance versus temperature characteristics in all the environments considered. We were able using a sensing device with a spin coated layer of the MWNT and screen printed silver electrode pattern to obtain a sensitivity of about

0.3%/^{o}C and linearity of about 15%FS.

An attempt has also been made to manufacture an array of devices using the same MWNT ink used in the single device examination above. However the method of spin coating of the MWNT used for single device fabrication proved to be inadequate. This is since the array of devices produced using spin coating suffered from lack of uniformity, which led to the current consideration of inkjet printing as an alternative technique. This resulted in an array of devices with much better uniformity, although much reduced sensitivity, which could be attributed to ineffective via formation as well as PDMS encapsulation techniques.

Keywords: Carbon Nanotubes, Singlewalled/Multiwalled Carbon Nanotubes, Temperature Sensor, Array of devices

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Chapter 1

Introduction

Skin is an organ of the integumentary system made up of multiple layers of epithelial tissues that guard underlying muscles and organs. As the interface with the surroundings, it plays the most important role in protecting against pathogens. Its other functions are thermal insulation and temperature regulation, sensation and vitamin D and B synthesis. Skin is considered one of the most important parts of the body. For sensation, the skin contains a variety of nerve endings that react to heat, cold, touch, pressure, vibration, and tissue injury [1].

Electronic skin (E-skin) is used to give robots the ability to touch and move objects with the appropriate force, one example which stands out is the ability to adjust the gripping force between a frying pan and an egg. Long term ambition of designers, is to be able to use E-skin with prosthetic limbs where the E-skin interfaces with the human brain directly.

Someya and his colleagues at the University of Tokyo are convinced that the functionality of E-Skin can be expanded to incorporate additional types of sensors. In their own words, in the near future it will be possible to make electronic skin with functions that human skin lacks. The additional sensing would include sensors for temperature, pressure, light, humidity, strain and even the sensors for ultrasonic sound. They recognised that elastic materials with carbon impregnation are an important step forward to realizing elastic electronics for robotics and other electronic devices, including sensing skin. They have used grinding of nanotubes with an ionic liquid to disperse evenly the nanotubes, which is certainly a novel technique that appears to show promise [2].

In 2010 Gerhard Domann and his colleagues in Würzburg announced their intention to design a cell phone which uses E-skin capability to start working from being switched off. As was mentioned in the article, the sensor consists of pyroelectrical and piezoelectrical polymers processed using screen printing. The sensor design incorporates the use of an organic transistor, also printed, and mainly used to strengthen the signal [3].

Ali Javey and his colleagues at University of California used nanowires made of tiny wires using inorganic materials such that a brittle material is turned into a flexible one such that it can be applied to robotics and prosthetic limbs [4].

Furthermore, due to inorganic materials used in sensor then it has reasonable characteristics and doesn't suffer from organic materials' weakness.

John Rogers and his colleagues at the University of Illinois designed a patch which consists of a flexible and stretchy lattice of sensor-laden circuits. It can be applied and removed like a temporary tattoo and sticks to skin without adhesives. It is designed for remote monitoring of health of patients. This design makes use of Van der Waals forces that the sensor to stick to skin [5]. The clever part of the design is that it uses conventional processing which means that mass production can happen quickly, however bringing down the price still needs to be done.

Smart shirts, or clothing made from smart fabric, have been made by several companies and so are in the market as first steps towards E-skin, including, Numetrex, Adidas, Alphyn Industries, Sensatex, SmartLife and Zephyr Technology. The SmartLife HealthVest uses technology originating from the University of Manchester based on knitted sensor structures which are multi -functional and integral to the garments manufacture. These soft sensors contain discreet electric and electronic components for monitoring physiological signs.

The LifeShirt by VivoMetrics was the first commercially available smartshirt and recorded ECG, respiration using inductance plethysmography, accelerometry, with optional plugin pulse oximetry, GSR, blood pressure, microphone and electronic diary capture. The data collection component of VivoMetrics LifeShirt System is a sleeveless undergarment that functions as a multichannel cardiopulmonary digital recorder. The shirt is made of hand-washable, reusable stretch-material into which are sewn an array of physiologic sensors to monitor 30+ vital signs. The individual being monitored can self-report symptoms, activities and medications into the PDA which then becomes part of the digital data stream. Any peripheral diagnostic device with digital output may be plugged into the serial port and its (their) measurements also become part of the digital data stream, e.g. pulse oximeter blood pressure, temperature, weight, etc. The data is stored on a module containing a data card that is incorporated into a customized Handspring worn on the patient's belt or carried in a pocket [6]. All these help in remote diagnosis and monitoring of patients without the need for regular visits to the doctors. This gives the doctors the ability to focus on more pressing cases.

The Sensatex Smart Shirt is manufactured by Sensatex, but was developed by the Georgia Institute of Technology. The shirt contains sensors that can be used to monitor vital signs such as heart rate, EKG, respiration, and blood pressure. To date this "Smart shirt" has not entered production [7]. This design was intended for soldiers to check their vital signs while in the field.

Chapter 2

Materials

2.1 Carbon Nanotubes (CNTs)

Carbon nanotubes are unique nanoscale structures with remarkable electronic properties stemming from their close relationship with graphite and from their one-dimensional characteristics. A nanotube can be considered as a graphene sheet that has been rolled up to make a seamless hollow cylinder. These hollow cylinders can be tens of micrometers long, but with diameters as small as 0.7 nm, thereby having a large surface area to volume ratio which is an important property for many applications. Singlewalled nanotubes (SWNT), having a cylindrical shell with only one atom in thickness, can be considered as the fundamental structural unit. Multiwalled nanotubes (MWNT) contain multiple coaxial cylinders about a common axis [8]. Iijima made the first reported observation of MWNT in 1991 when he saw tiny tubular structures while looking at carbon soot in a tunneling electron microscope [9]. This discovery has started a chain reaction of research in many universities around the world including Seoul National University.

Depending on the geometric arrangement of carbon atoms, the nanotube will exhibit either semiconducting or metallic characteristics [8]. Defect free nanotubes can act as one-dimensional quantum wires where electron scattering occurs only at the nanotube-contact interface [10], and, because of the strong carbon-carbon bonds that make up their structure, they can carry the highest current density of any material before they break. This makes them ideal for many applications.

To explain the electrical characteristics of carbon nanotubes, it is useful to first explain the electrical behaviour graphene, their two dimensional analogue. Graphene is a single planar sheet of sp^2 bonded carbon atoms arranged in a honeycomb pattern as shown in Fig. 1(a) below. A unit cell for graphene is shown in Fig. 1(b) with its basis vectors. The primitive unit cell for graphene contains two carbon atoms, each of which contributes one electron to the valence band. Therefore, there are two valence electrons per unit cell and graphene has a filled valence band, making it a semiconductor. However, because of symmetric effects, the valence and conduction bands meet at the edge of the Brillouin zone at the K point, making graphene a zero band-gap semiconductor that behaves metallic [8].

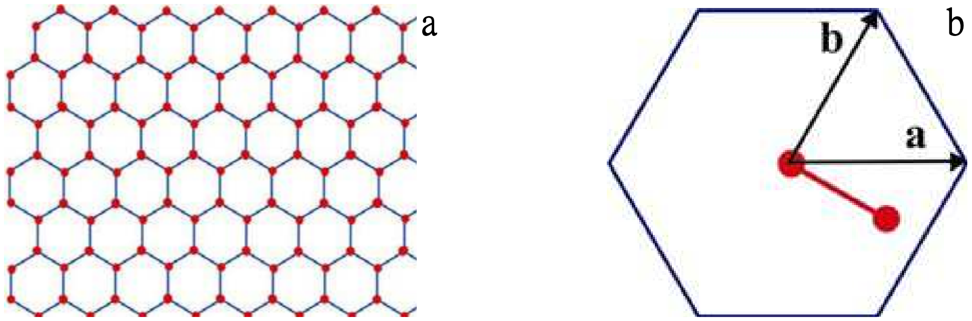

Figure 1 Graphene (a) sheet of graphene (b) unit cell

A SWNT is constructed from a section of a graphene sheet, as shown in Fig. 2 below. The shaded section of the picture represents the portion of the graphene sheet that will be rolled up to make the nanotube. The vector C = na+mb, called the chiral vector, forms the nanotube's circumference. When the nanotube is rolled up, the chiral vector will originate and terminate on the same carbon atom. In this description, a and b are primitive vectors for the graphene sheet and n and m are integers [11]. Therefore, when the nanotube is formed, the cylinder will be completely seamless. The nanotube unit cell is enclosed in the box formed by the vectors C and T. Once the nanotube has been rolled up, it essentially is a 1D crystal with spacing T between unit cells.

Theoretical calculations have shown that the electronic properties of carbon nanotubes are very sensitive to their geometric structure [12-14]. Although graphene is a zero-gap semiconductor, theory predicts that carbon nanotubes can be either

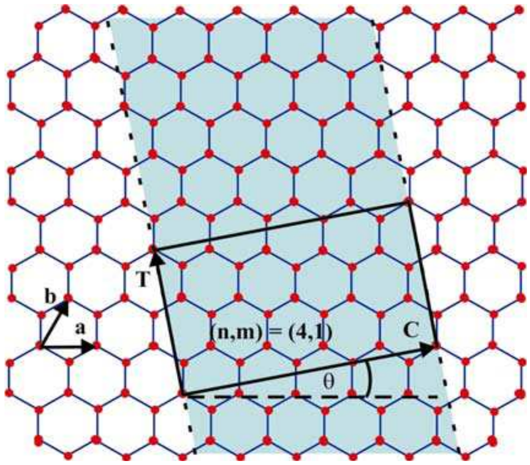

Figure 2 Formation of a single walled carbon nanotube from a graphene sheet

metallic or semiconducting with different energy gaps, depending very sensitively on the indices (n,m). For (n,n) or (n,3j–n), where j is an integer, the nanotube will be metallic. For all other (n,m), the nanotube will exhibit semiconducting characteristics. This gives a higher possibility to obtain semiconducting nanotubes.

Heat transport properties of CNTs have also been reviewed from standpoint of the phonon-conduction mechanisms on the basis of the thermal conductance and/or thermal conductivity. At low temperatures, phonon conduction is ballistic through the entire body of the SWNT, leading to universal quantization in the thermal conductance. The quantized nature persists despite the presence of structural defects. As the temperature is increased, the length of the phonon mean free path becomes comparable to that of the SWNTs, and phonon conduction ceases to be ballistic. As such a marked reduction is observed in the thermal conductivity due to defects. The heat transport behaviour changes from quasiballistic to diffusive at temperatures above room temperature. MWNTs further show the characteristic temperature dependence of the thermal conductivity due to the van der Waals interaction between the tube walls [8].

2.2 Polydimethylsiloxane (PDMS)

Long-term, reliable protection of sensitive circuits and components is becoming more important in many of today's delicate and demanding electronic applications. Silicone encapsulants provide unparalleled protection for a variety of electronic modules and devices. Silicones function as durable dielectric insulation, as barriers against environmental contaminants, and as stress relieving shock and vibration absorbers over a wide temperature and humidity range. In addition to sustaining their physical and electrical properties over a broad range of operating conditions, silicones are resistant to ozone and ultraviolet degradation and have a good chemical stability [17].

Silicone encapsulants may be either room temperature or heat cured. Room temperature curing method was used in this thesis for single device fabrication, whilst curing at 60^{o}C for 4 hours for the array device.

PDMS is the silicone used for encapsulation in this thesis. PDMS is the most widely used silicon based organic polymer and is particularly known for its unusual rheological properties. PDMS is optically clear and is in general considered inert, non toxic and non flammable [16]. Its applications range from contact lenses and medical devices to elastomers used in shampoos, caulking, lubricating oils and heat resistant tiles. It is usually very resistant to mixing with water and so is often a component in sealers.

Silicone elastomers should be operational over a temperature range of -45 to 200 C for long periods of time. However at both ends of spectrum then behaviour may become unpredictable. At high temperatures the durability of cured silicones is time and temperature dependent however the testing that is carried out in this thesis was up to the maximum of about 110 C so there was no risk of abnormal behaviour [17].

2.3 Indium Tin Oxide (ITO)

It is an n-type degenerate semiconductor routinely used as an electrode. When applied as a coating to glass, mylar or other transparent surface, ITO create conductive, highly transparent surfaces which reflect infrared rays while allowing visible and ultraviolet lights to pass [18]. Oxide-coated glass meets a wide range of demanding environmental requirements, due in part to the superior hardness and durability of the coatings. Despite oxide coatings being readily etched, they are resistant to most commercial solvents.

ITO coatings are used in a wide variety of applications such as solar collector panels, photovoltaic cells, low E-residential and commercial windows, LCD glass, aircraft windshields, highly efficient low pressure sodium lamps and transparent antistatic panels.

We use ITO electrodes for initial electrode patterns of our device which were out-sourced, fabricated using vacuum techniques and so has good uniformity, it was therefore used for testing of the CNT inks in the different environments.

Chapter 3

Temperature Sensors

3.1 Commercial Sensors

Temperature sensors can be classified into contact and non contact sensors. The contact sensors include thermocouples and resistance temperature detector (RTD). The latter produces varying resistance values, and so maybe classified as resistance wire RTDs and thermistors [19].

RTD is a general term for any device that senses temperature by measuring the change in resistance of a material. An RTD probe made commercially is an assembly composed of a number of different elements including, a resistance element, a sheath, lead wire and a termination or connection. The sheath immobilizes the element, protecting it against the environment to be measured [20].

The most common element used for RTDs is platinum. The platinum coil is available in several resistance ohm values with 100 ohms being the most used value commercially by many companies.

Platinum RTD elements take either of two forms: wire-wound or thin film. Thermometrics Corp. wire-wound elements are made by winding a very fine strand of platinum wire into a coil until there is enough material to equal 100Ω of resistance. The coil is then inserted into a mandrel and powder is packed around it to prevent the sensor from shorting and to provide vibration resistance. This is a time-consuming method and all work is done manually under a microscope, but the result is a strain-free design [21].

Another type of sensors discussed here are thermistors, which are thermally sensitive resistors whose prime function is to exhibit a large, predictable and precise change in electrical resistance when subjected to a corresponding change in temperature. They are similar to RTDs but which are fabricated from metal oxide semiconductor which is encapsulated in a glass or epoxy bead. Negative Temperature Coefficient (NTC) thermistors exhibit a decrease in electrical resistance when subjected to an increase in body temperature and Positive Temperature Coefficient (PTC) thermistors exhibit an increase in electrical resistance when subjected to an increase in body temperature. Because of their very predictable characteristics and their excellent long term stability, thermistors are generally accepted to be the most advantageous sensor for many applications including temperature measurement and control [22].

Since the negative temperature coefficient of silver sulphide was first observed by Michael Faraday in 1833, there has been a continual improvement in thermistor technology. The most important characteristic of a thermistor is without question its extremely high temperature coefficient of resistance. Modern thermistor technology results in the production of devices with extremely precise resistance versus temperature characteristics, making them the most advantageous sensor for a wide variety of applications [22].

A final type of temperature sensor discussed here is a thermocouple, which is a sensor that has at least two junctions, a measurement junction and a reference junction. The reference junction is created where the two wires connect to the measuring device. The simple relationship between the temperature difference of the joints and the measurement voltage is only correct if each wire is homogeneous. With an aged thermocouple this is not the case [23].

Thermocouples, unlike the sensors mentioned above, can produce current, which means it can be used to drive some processes directly, without the need for extra circuitry and power sources. The electrical energy generated by a thermocouple is converted from the heat which must be supplied to the hot side to maintain the electric potential. A continuous flow of heat is necessary because the current flowing through the thermocouple tends to cause the hot side to cool down and the cold side to heat up (the Peltier effect). For typical metals used in thermocouples, the output voltage increases linearly with the temperature difference over a bounded range of temperatures. For precise measurements or measurements outside of the linear temperature range, non-linearity must be corrected for [24].

Thermocouples are in most cases made by welding which is simple enough and insulation is required either to prevent oxidation or to prevent contamination depending on materials used. It is made for different applications and so materials used maybe different for each which means that price range maybe relatively high.

A thermopile is a thermoelectric device that consists of an array of thermocouples connected in series. It is widely used in non-contact temperature measurement applications and temperature monitoring systems. Thermopiles detect the temperature of an object by absorbing the infrared (IR) radiation that emits from the object's surface. Most of the thermopile detectors are equipped with a black body surface for effectively absorbing the IR radiation [23].

Many companies such as Sensoscientific and Veriteq are targeting niche markets such as in hospitals and food packaging companies where online or software monitoring may be very useful especially since hygiene is to be expected [25, 26].

3.2 Research Sensors

As for the sensors that are considered in research, then it appears that there are two groups, one group considered vacuum techniques for manufacturing their sensors and can achieve small dimensions, but produce a lot of waste and take much time and money. The other group considered solution processing to manufacture sensors which can appeal to mass market and more specifically for large area applications such as E-skin.

3.3 Our Sensor Design

This section begins by considering each element of the design of the single temperature sensor. It ends with a discussion of the design of the array of devices.

3.3.1 Electrode Design

When I started this project, I inherited my predecessor's electrode design which consisted of two parallel lines of ITO or silver which is depicted in Fig. 3 (a) below. This design is simple and was used mostly when properties of CNT were investigated. However for use as a temperature sensor, interdigitated electrode pattern was considered. Interdigitization of electrodes is important since sensors are getting smaller and are often required to operate at low voltages. Interdigitized electrodes increase the area of interaction with the temperature-sensitive material which therefore reduces the voltage required for sensing. However there is an art to design of Interdigitized electrodes and one which would have required time beyond what was achievable [26]. In this thesis the design investigated was shown in Fig 3 (b) below and it gave results that were as expected in terms of growth of signal (i.e. higher current), but with lower sensitivity, which may be due to lack of optimization of design.

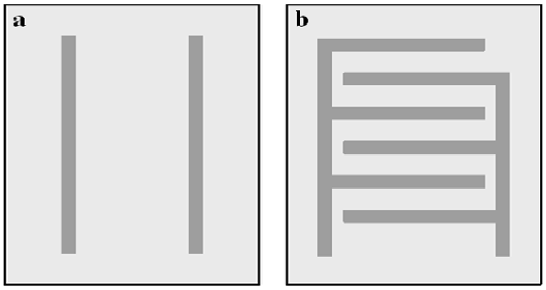

Figure 3 Two electrode designs (a) simple (b) interdigitated

Both electrode patterns were fabricated using different methods and materials, including silver electrodes using screen printing or inkjet printing (solution process), and ITO electrode patterned using sputtering (vacuum process).

The electrode materials used are known for not having resistances that vary with temperature did (i.e. small temperature coefficient of resistance (TCR)). The resistance-change factor per degree Celsius of temperature change is called the temperature coefficient of resistance, represented by the Greek lower-case letter "alpha" (α). Figures of specific resistance are always specified at a standard temperature (usually 20° or 25° Celsius). A positive coefficient for a material means that its resistance increases with an increase in temperature. Pure metals typically have positive temperature coefficients of resistance. Coefficients approaching zero can be obtained by alloying certain metals. A negative coefficient for a material means that its resistance decreases with an increase in temperature. Semiconductor materials (carbon, silicon, germanium) typically have negative temperature coefficients of resistance. The formula used to determine the resistance of a conductor at some temperature other than what is specified in a resistance table is as shown below alongside TCR values of electrode materials used [27].

$$\mathbf{R = Rref\,[1 + \alpha(T - Tref)]} \qquad \textbf{(3-1)}$$

R = Conductor resistance at temperature T

R_{ref} = Conductor resistance at reference temperature Tref

α = Temperature coefficient of resistance for the conductor material

T = Conductor temperature

T_{ref} = Reference temperature that α is specified at

Table 1 TCR values of electrode materials used in sensors

Electrode Material	**TCR**	
Silver	2×10^{-4}	[27]
ITO	4×10^{-3}	[28]

3.3.2 Temperature-sensitive Material

The material used for temperature sensing is MWNT. Carbon nanotubes (CNT) are unique nanoscale structures with remarkable electronic and mechanical properties. Since their discovery by Iijima in 1991 [9], many research groups have been fabricating many different devices, such as, inkjet printed CNT for TFT application [29], screen printed CNT for electrochemical sensor application [30], and inkjet printed CNT for fabrication of electrode [31].

The aim here was to investigate materials that could be deposited using solution processing. Several available candidates were investigated which are normally used for different application within our group such as silver (inkjet-printed or screen-printed used as electrode material) and PEDOT (spin coated used in OLED generally). The TCR values for the two materials considered alongside CNT are included in table 2 below.

Two CNT inks were investigated in this thesis, one of which was used for the final device. One of these inks was a SWNT ink obtained from Nanostructured & Amorphous Materials Inc. [length: 5-30 µm, diameter: 20-35 nm]. The other ink was a MWNT ink obtained from Cluster Instruments Co., Ltd. [length: 5-30 µm, diameter: 1-2nm].

Table 2 TCR values of materials considered as temperature sensitive materials

Temperature Sensitive Material	TCR	
Silver	2×10^{-4}	[27]
PEDOT:PSS	1.5×10^{-3}	[32]
CNT	2.4×10^{-3}	

3.3.3 Substrate

Two types of substrates were considered in this thesis and these are glass and PET. The use of glass was the starting point where ITO was used as electrode material, sputter-coated outsourced [Freemtech]. However given that we were aiming for flexibility then plastic is the ideal material and is so was used in the final device. Graphs in the discussion chapter highlight the differences between the different substrates.

3.3.4 Encapsulation

The encapsulating material used was PDMS, and its importance in encapsulation is highlighted in the previous chapter. It is a material used very often for encapsulation by our group as well as others. It is easy to prepare and apply as well as cure which makes the ideal candidate for mass production, which is at the heart of this thesis.

3.4 Polydimethylsiloxane (PDMS)

The sensor researched in this thesis, unlike the commercial ones mentioned above, is made of an organic temperature sensitive material and using solution processing. It is designed to be used for E-skin which requires less precision, flexibility, and ready to be made into an array. These factors were not targeted by the commercial sensors mentioned above which target more accurate applications where a single degree makes the world of difference. Table 3 below highlights more clearly the differences between the commercial sensors and the one researched in this thesis.

Fig. 4 below shows graphically how our sensor compares to other research groups' sensors as well as commercial sensors from two companies (U.S. Sensors, Thermometrics Corp.). We are considering different types of temperature sensing with two main parameters in mind (sensitivity and linearity), which are summarized in table 4.

It is clear from Fig. 4 and table 4 above that our sensor (fabricated using screen printed silver electrodes with MWNT ink, the decision for which will be discussed in the last chapter of this thesis) fares well overall, despite it has the lowest sensitivity. These results are remarkable considering that our sensor was the only one to be made using solution processing whilst the other two were fabricated using conventional and vacuum techniques.

Table 3 Comparison of our sensor with known commercial temperature sensors

	Commercial			Research
Attribute	Thermocouple	RTD	Thermistor	CNT sensor
Cost	Low	High	Low	Low
Temperature Range	Very wide -350°F +3200°F	Wide -400°F +1200°F	Short to medium -100°F +500°F	Limited tested range +86°F +212°F
Long-term Stability	Poor to fair	Good	Poor	Fair
Accuracy	Medium	High	Medium	Low (due to O_2 effects)
Repeatability	Poor to fair	Excellent	Fair to good	Requires further testing
Sensitivity	Low	Medium	Very high	Medium
Linearity	Fair	Good	Poor	Good
Size/Packaging	Small to large	Medium to small	Small to medium	Small to medium
Flexibility	Low	Low	Low	Good
Complexity of Production	Low	High	Low	Low
Array Formation	Good	N/A	Fair/Good	Good

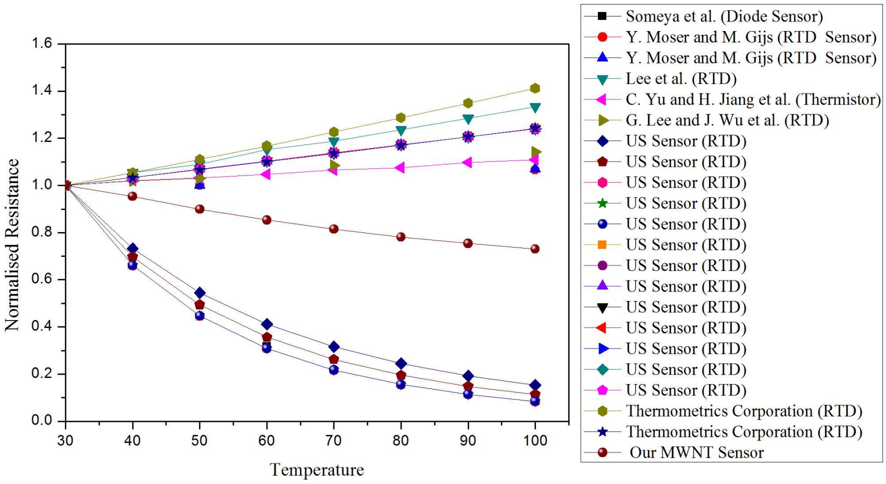

Figure 4 Comparison of our sensor with research and two commercial sensors

Table 4 Comparison of our sensors with one commercial and one research sensor, each chosen for their best sensitivities

	Sensitivity %/ºC	**Linearity (%FS)**
Research Sensors	0.4	<10
Commercial Sensors	>1	<30
Our Sensor (screen printed)	0.3	>15

Chapter 4

Methodology

This is divided into two main categories including single device and array of devices methodologies.

4.1 Single Device Methodology

This will include all the steps in detail.

4.1.1 Substrate Preparation

This is done in two steps:

* Substrate cleaning included three steps done in sequence (Acetone, IPA, and DI-Water) each of which lasted 20 minutes.

* UV/O_3 is required to increase adhesion of CNT on surface. This process was carried out for 15 minutes for glass substrates and 5 minutes for plastic substrates. These figures were chosen since they gave the best cover of CNT on sample.

4.1.2 Electrode Patterning

Different techniques were used to create electrode patterns using different materials, including:

4.1.2.1 ITO electrode

It was deposited using sputtering (PVD) and patterned using photolithography to give the two patterns shown in Fig. 3. These samples were outsourced from [Freemtech]. This process created a very accurate pattern of ITO on glass and was used mainly for investigation of the temperature sensitive material, CNT as will be covered in the discussion. This method of deposition is not ideal for mass production since it is expensive and so not ideal for large area electronics for which this device is intended for.

4.1.2.2 Silver electrode

This electrode was deposited using two different techniques which are far more adaptable for large area electronics. These methods are ideal for our purpose and initially for ease of manufacture then screen-printing was investigated, however it was soon found to be more accurate to use inkjet printing. However another problem occurred, for when the silver ink was changed (due to the ink running out) it required change of settings which compromised the quality of the print and so reverting to screen-printing was vital.

* Screen printing is a printing technique that uses a woven mesh to support an ink-blocking stencil widely used in different industries. The attached stencil forms open areas of mesh that transfer ink or other printable materials which can be pressed through the mesh as a sharp-edged image onto a substrate. A roller or squeegee is moved across the screen stencil, forcing or pumping ink past the threads of the woven mesh in the open areas [33].

* An inkjet printer is a type of computer printer that creates a digital image by propelling droplets of ink onto paper. Most commercial and industrial inkjet printers and some consumer printers use a piezoelectric material in an ink-filled chamber behind each nozzle instead of a heating element. When a voltage is applied, the piezoelectric material changes shape, which generates a pressure pulse in the fluid forcing a droplet of ink from the nozzle. Piezoelectric inkjet is

the one available in our labs, it allows a wider variety of inks than thermal inkjet as there is no requirement for a volatile component, and no issue with kogation (build-up of ink residue), but the print heads are more expensive to manufacture due to the use of piezoelectric material [34]. Despite what the companies state, the new silver ink used in our labs has been suffering from formation of bubbles as well as clogging which are both non ideal for fabrication of consistent samples.

4.1.3 CNT Deposition

CNT deposition was done using spin coating which is a solution process ideal for large area electronics. Because cost/square centimeter is such a major driver for microelectronic applications, established methods for low-cost manufacture are of great interest. Solution processing has received significant attention because it can result in the production of a range of devices using different techniques for deposition of ink [35], one of which is spin coating used in this thesis. Spin coating is a procedure used to apply uniform thin films to flat substrates. In short, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. So, the higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the concentration of the solution and the solvent. Two speeds were used for the spreading of the CNT ink as follows:

* Initial slow speed of 500 rpm for 5 seconds, necessary for initial spread of ink on surface and ensure better overall uniformity.

* Final high speed of 8000 rpm for 30 seconds, which produces the final layer of varied thickness as will be discussed in the topography section of this thesis.

4.1.4 Annealing

It is the heat treatment that was used to remove any excess solvent that was in the ink. It was done for a short time of about 10 minutes at a temperature of about 100°C. The effect of annealing is shown in Fig. 5 below, in which it is evident that the sensitivity appears to decrease, however for the case of MWNT then linearity appears to improve. However heating is an important step to ensure that repeatability is obtained.

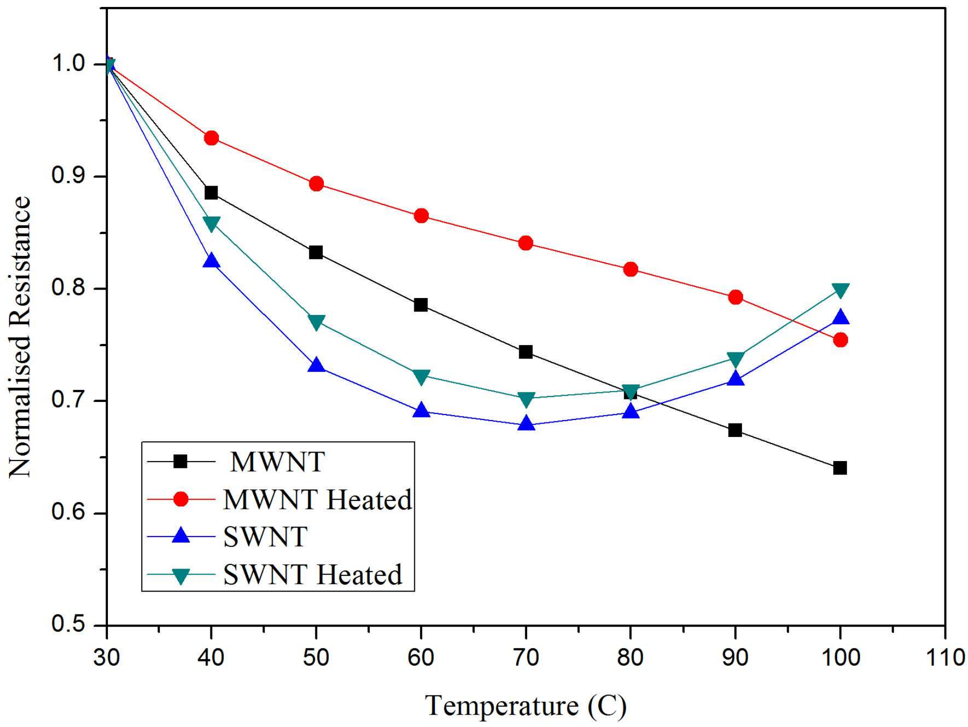

Figure 5 Effect of annealing on characteristics of sensor

4.1.5 Encapsulation

As was mentioned in the previous chapter, PDMS is the silicone used for encapsulation. PDMS is the most widely used silicon based organic polymer and is particularly known for its unusual rheological properties. PDMS is optically clear and is in general considered inert, non toxic and non flammable. This makes it ideal for E-skin application.

PDMS was prepared using elastomer and a curing agent at a ratio of (10:1), which were then folded together for about 10 minutes and then placed in the desiccator for about 30 minutes or until the bubbles were completely removed. It was then poured over sample and placed in desiccator again for about 2 days to be cured at room temperature and so created a good encapsulating layer for the CNT devices. All of the above steps are summarized in Fig. 6 below.

4.1.6 Measurement

The resistance of each of the samples prepared using the method above were then measured using Agilent 4155C at each decade within the temperature range of (30–100)^{o}C, whereby heat was applied using a chuck. This measurement technique was applied in three different environments:

* Atmosphere
* Argon chamber
* Vacuum chamber

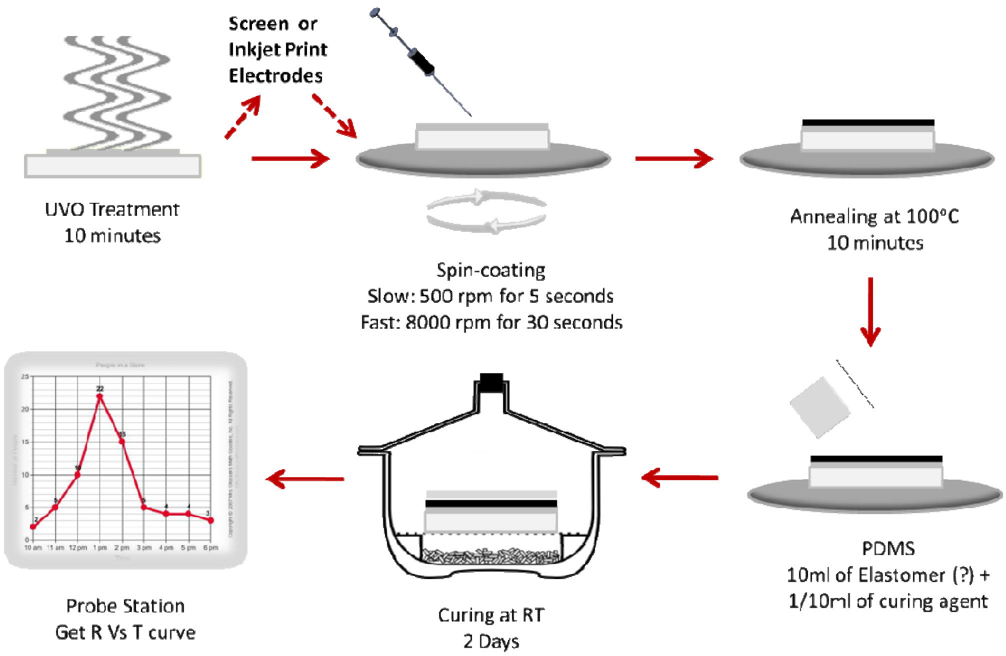

Figure 6 Single device manufacturing process

4.1.7 Topography

In addition to measurements using the above analyzer, it appeared to be necessary to also consider the nature of the surface of the MWNT and SWNT inks which are considered in this thesis. Fig. 7 (a, c, and e) all show MWNT ink, its thickness, density, as well as its roughness. As for Fig. 7 (b, d, and f) then they show similar characteristics but for the SWNT ink. When comparing the two inks with the help of these images then it may be fair to assume that the thickness of MWNT layer is greater, rougher but less dense.

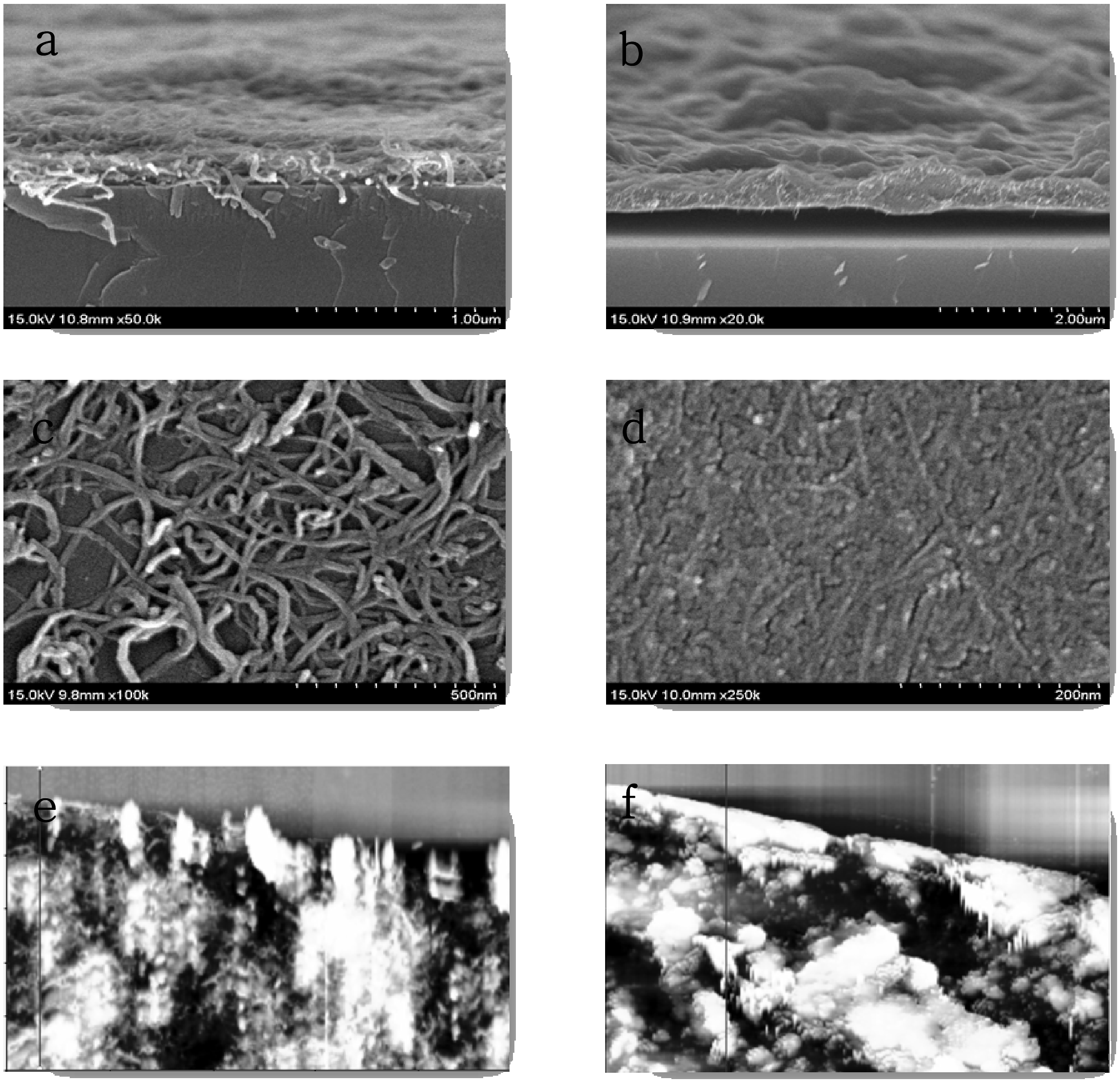

Figure 7 SEM used to view MWNT in (a and c) and SWNT in (b and d), whilst AFM is used to view MWNT in (e) and SWNT in (f)

4.2 Array of Devices Methodology

4.2.1 Substrate Preparation

Since the substrate used was PET then it was simply UV/O_3 treated for 5 minutes, after which electrode patterning can begin.

4.2.2 Electrode Patterning

Since silver is the material used on the PET substrate then a solution process of either inkjet or screen printing can be used. In our case, screen printing was used since the quality of the pattern fabricated using inkjet printing was poor, as was discussed before. It is important to note that, two layers need to be printed since we are now dealing with an array of devices.

4.2.3 CNT Deposition

It was done using spin coating, with the same two speeds as for the single device. The only difference this time is that a bigger stage needed to be used due to the increase of the size of the substrate.

4.2.4 Via Formation

This step was done using a drill to drill through the two layers as is shown in Fig. 8 below. The holes created were then filled using silver ink which enabled contact between the two layers.

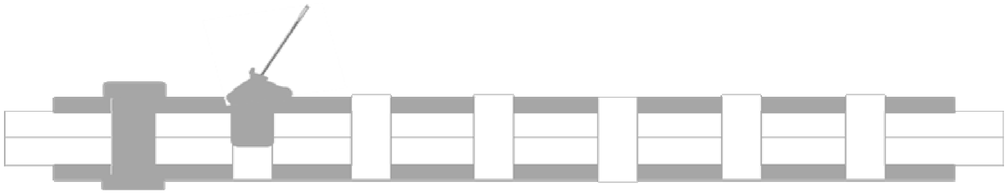

Figure 8 Via formation

4.2.5 Annealing

Same as was done for the single device was done here again.

4.2.6 Encapsulation

PDMS was prepared using elastomer and a curing agent at a ratio of (10:1), which were then folded together for about 10 minutes and then placed in the desiccator for about 30 minutes or until the bubbles were completely removed. It was then poured over sample and placed on a hot plate to be cured for 4 hours at 60^{o}C.

4.2.7 Measurement

The array of devices were attached to wires that enabled the use of a passive matrix that in turn uses a power supply and Keithley 2400 analyzer which in turn enables collection of data. Heat was applied by using a hot plate or object depending on the nature of the test.

Chapter 5

Results and Discussion

This section will be divided into two distinct yet related parts, the first of which begins the investigation of the resistance variation of a CNT thin layer with temperature in different environments and ends with a simple temperature sensor design investigation and feasibility study. The second part includes the feasibility study of an array of sensors printed on plastic using the CNT as a temperature sensitive material.

5.1 Single Device Methodology

This section will start with the investigation of sensor design and then moves into investigation of CNT as a temperature sensitive material.

5.1.1 Sensor Design Optimization

The design that has been used and considered in the lab group so far was mostly for the sake of a feasibility study of the sensor for E-skin design. However in this section the design of the electrode is considered as was mentioned in Chapter (3) which highlights that interdigitization of electrodes is an important step for the increase of the signal. Fig. 3 highlights the change from conventional electrode pattern to interdigitated one. This design was tried and the results are shown in Fig. 9.

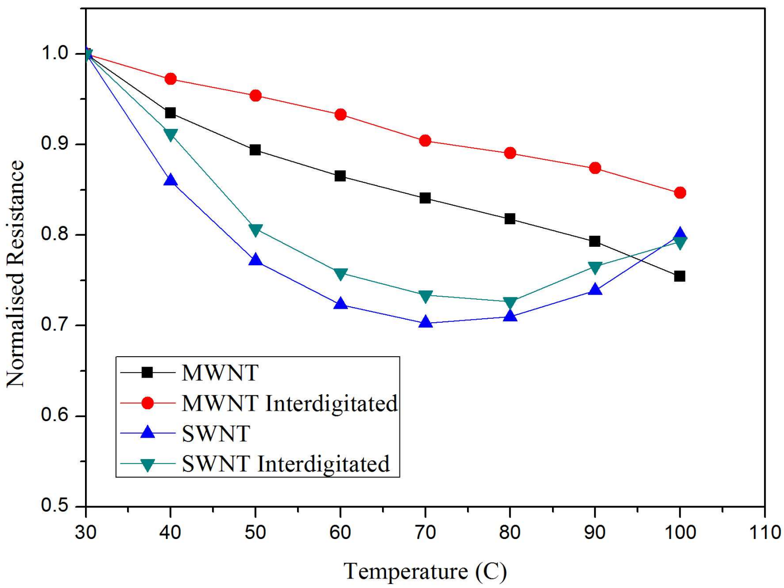

Figure 9 Effect of interdigitated electrodes

The graph shows that the signal is in fact much higher for the interdigitated electrode design; however it is also obvious from comparing the graphs that sensitivity is reduced by using interdigitated electrode design. This design could have been optimized further as was mentioned in Chapter (3) but due to time constraints, this can only be done in future projects.

5.1.2 CNT as a temperature sensitive material

In this section, two different points are investigated; the first is whether the environment in which the sensor is tested in affects its performance. Similar tests have been carried out by other researchers although normally on single SWNT tubes manufactured and treated using vacuum techniques, so it is to our knowledge that no tests have been done on SWNT and MWNT layers deposited using solution processing. The second is whether the type of ink used affects performance. Eventually, the type of ink is chosen that gives the best method for ensuring stability.

5.1.3 Effect of Environment

In this section, two sets of devices with the same electrode pattern, one of which is covered with SWNT and the other covered with MWNT, are tested using a probe station in three different environments as is explained below:

5.1.3.1 Atmosphere

In this case the samples mentioned above were prepared and tested at atmosphere. The samples were sequentially examined using the probe station, where the voltage was set to sweep between -10 V to +10 V and so measure the current flowing between the two electrodes.

Fig. 9 shows that sample covered with MWNT appears to behave more like a semiconductor, such that the temperature coefficient of resistance is negative, the resistivity decreases with rise of temperature. The reason for this behaviour is that for semiconductors the number of mobile carriers is very small and increases appreciably with rise of temperature [27].

As for the sample covered with SWNT then its behaviour appears to change from being semiconductor to being a metallic conductor at about 70^{o}C. From this we can make an initial assessment that the sample covered with MWNT is the better candidate for temperature sensing due to its reasonable linearity.

5.1.3.2 Argon

The two different inks (i.e. SWNT and MWNT) were prepared within an argon chamber and then subsequently tested within same chamber. Fig. 10 below shows the results obtained from this test

It is evident that SWNT appears to behave more like a metallic conductor right from 30^{o}C, which is very different from the result obtained in an atmospheric environment. As for MWNT then it seems to behave still more like a semiconductor except with a slightly lower sensitivity than before.

These results show that there is a level of dependency on nanotube interactions with surrounding gases be it of different levels depending on type of ink. In this case it should be highlighted that O_2 is not negligible in fact it was of a value of about 17.5% ppm.

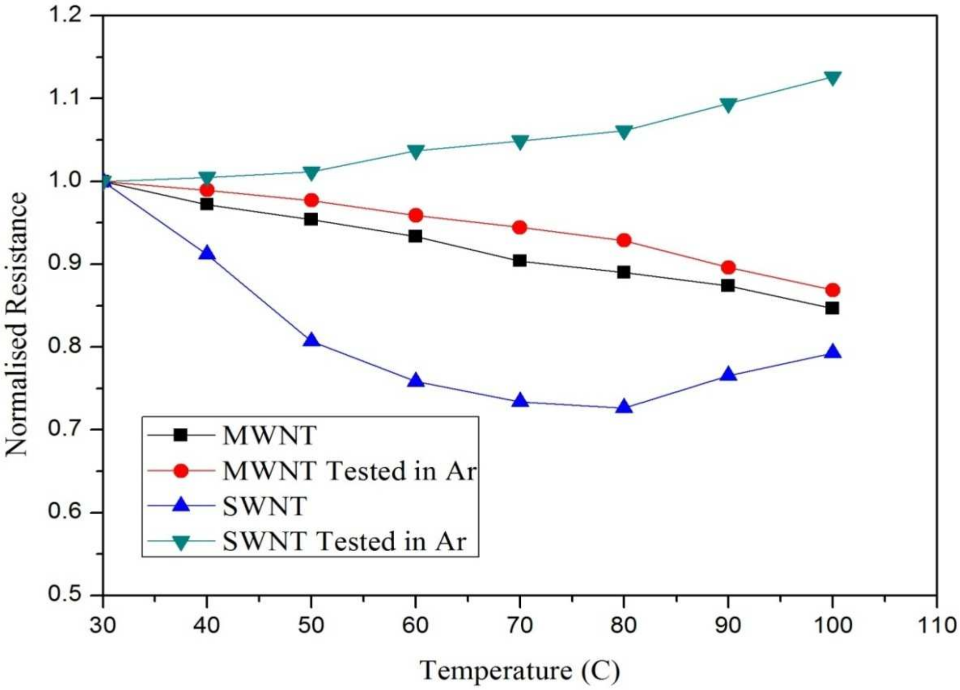

Figure 10 Effect of testing in an Ar environment

5.1.3.3 High Vacuum

As before two samples, each of which represents a different ink (i.e. SWNT and MWNT). The samples were prepared in an atmospheric environment and then tested in a high vacuum chamber at a pressure of about 2×10^{-5} mbar which is initially around 30^{o}C. It took about 15 mins for pressure to reach the value mentioned. Fig. 11 below shows results given from the test, which highlight that SWNT didn’t experience any change in behaviour but was behaving as a metallic conductor from the beginning, which emphasized the effect of the surrounding gases [15]. However, MWNT seemed to show similar behaviour to the sample tested in Ar chamber.

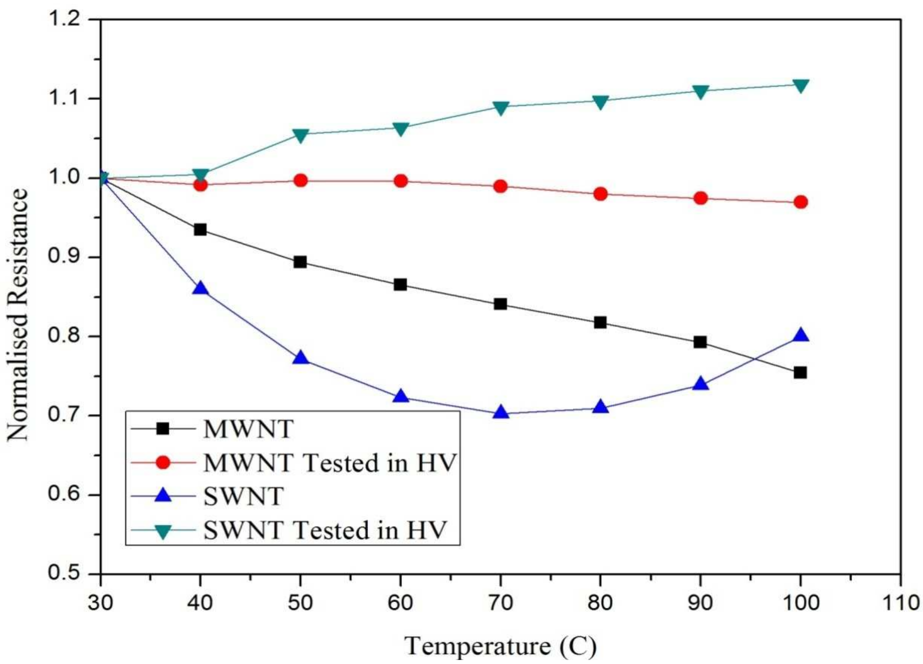

Figure 11 Effect of testing in a high vacuum environment

5.1.4 Effect of Encapsulation

Encapsulation is necessary for different electronic circuit boards to keep the board same from environmental effects (i.e. humidity, water…etc) and scratching of sensor while usage of sensor. It will become obvious when considering the graphs below that encapsulation indeed affects the sensitivity of the sensor.

5.1.4.1 Glass Encapsulation

The two different inks (i.e. SWNT and MWNT) were prepared in an atmospheric environment and then subsequently encapsulated within N_2 chamber and then tested within atmospheric environment. Fig. 12 below shows the behaviour obtained from this test.

It is evident from the graph that MWNT appears to have similar semiconducting characteristics but with much reduced sensitivity. As for SWNT then it appears to have more of a semiconducting characteristic.

However it should be noted that the glue used to enable encapsulation, started to melt at the higher temperature which may have affected the results.

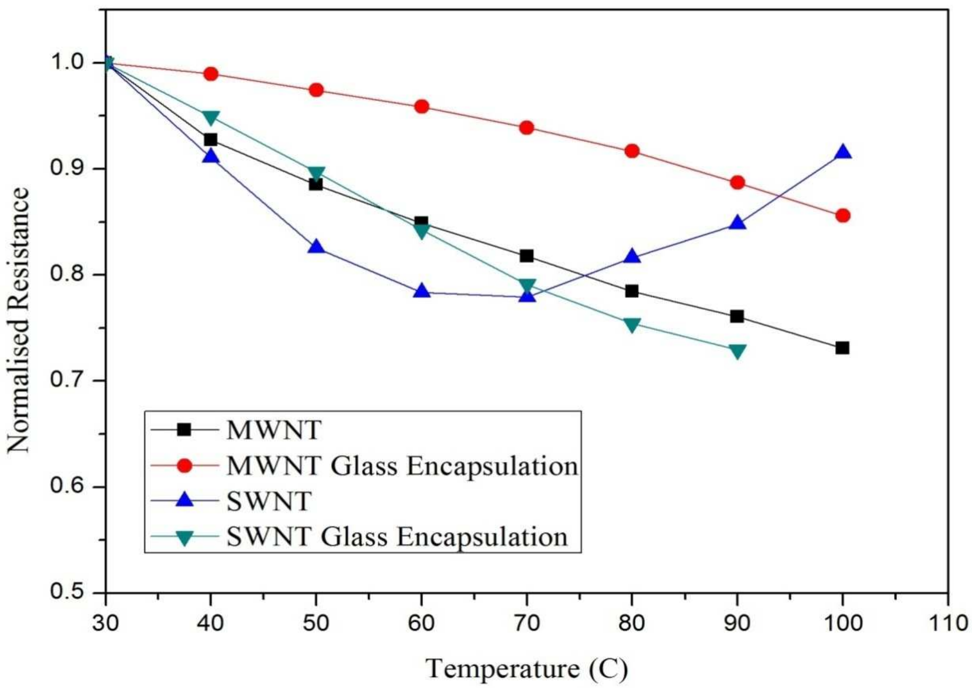

Figure 12 Effect of glass encapsulation

5.1.4.2 Effect of PDMS Encapsulation

Two samples were again prepared and tested in an atmospheric environment but with PDMS encapsulation as was explained in the methodology. The effect of this encapsulating layer is obvious from Fig. 13 below. MWNT characteristics seem to be still semiconducting-like but with reduced sensitivity. On the other hand, SWNT characteristics still has similar characteristics to the one obtained when testing in atmospheric environment, but with increased sensitivity within the range (30 – 70)^{o}C.

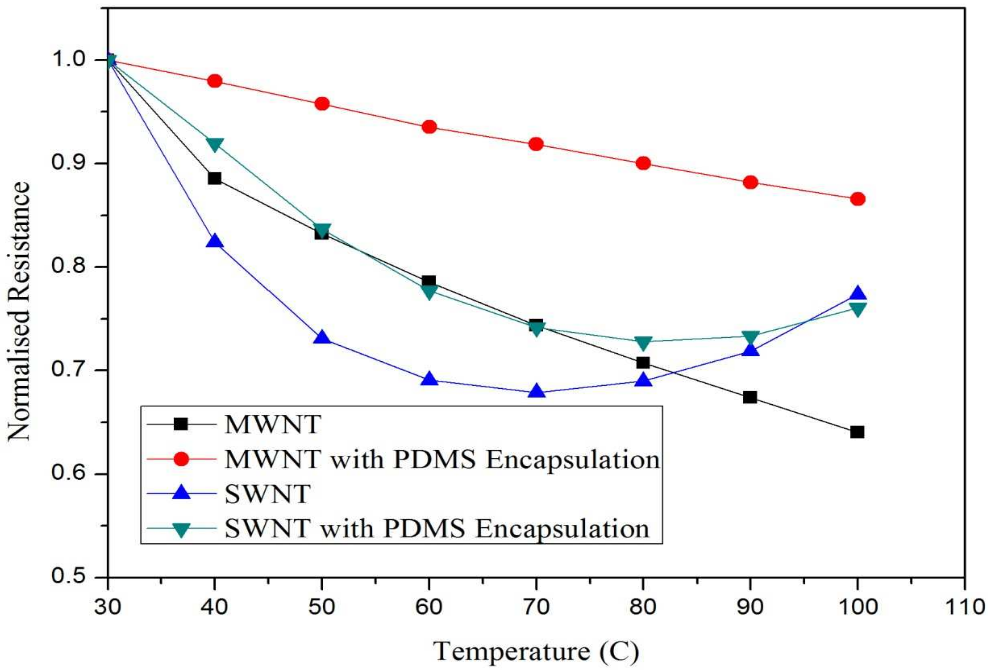

Figure 13 Effect of PDMS encapsulation

5.1.5 Effect of Substrate

There were two obvious investigations as was discussed above, the first considering the characteristics of CNT resistance change due to temperature change, whilst the second considers the sensor characteristics and the ability to obtain a design and method suitable for mass production. For the study of CNT, then glass substrates were suitable since flexibility and mass production was not an important consideration. However, for the investigation of sensor design and its applicability for mass market then plastic substrate is the targeted for use.

Fig. 14 below shows the results obtained for MWNT sensors with the same Ag electrode design but using different substrates. It is obvious from the graph that there is but little variation between the two results, which may even be attributed to errors in the printing process or heating equipment while testing.

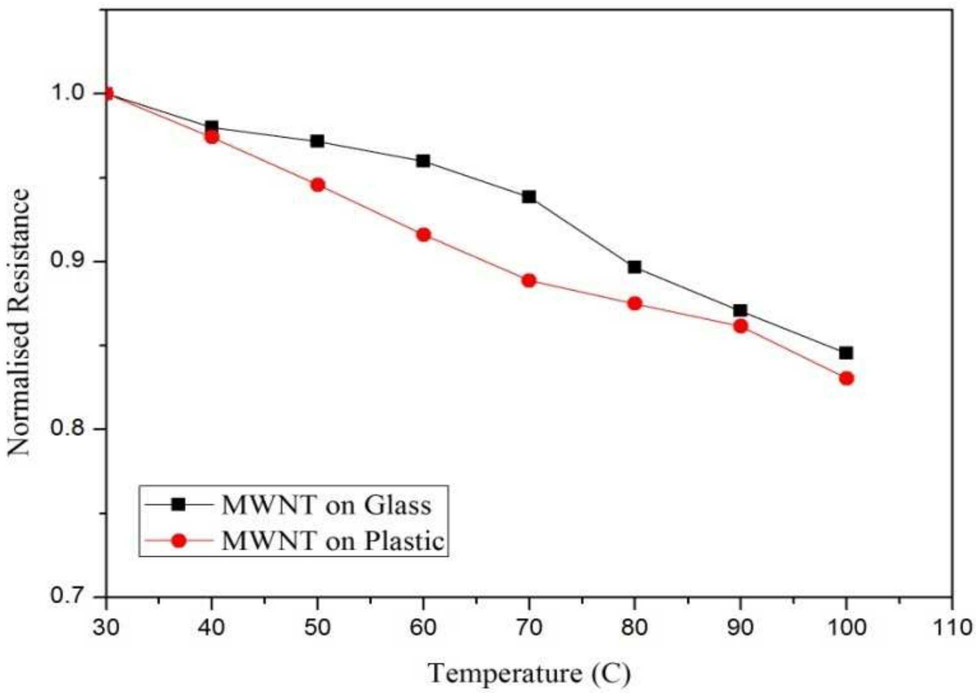

Figure 14 Effect of substrate type

5.1.6 Effect of Electrode Material and Electrode Production Technique

Two different electrode materials have been used, usually ITO on the glass substrate (deposited using vacuum techniques in a manufacturing facility) and silver on plastic, since it is very easy to obtain the silver pattern on plastic substrate using screen and inkjet printing. Fig. 15 below show samples with MWNT using the two of electrode materials on glass substrates. It again shows very little effect as was the case when substrate type was varied.

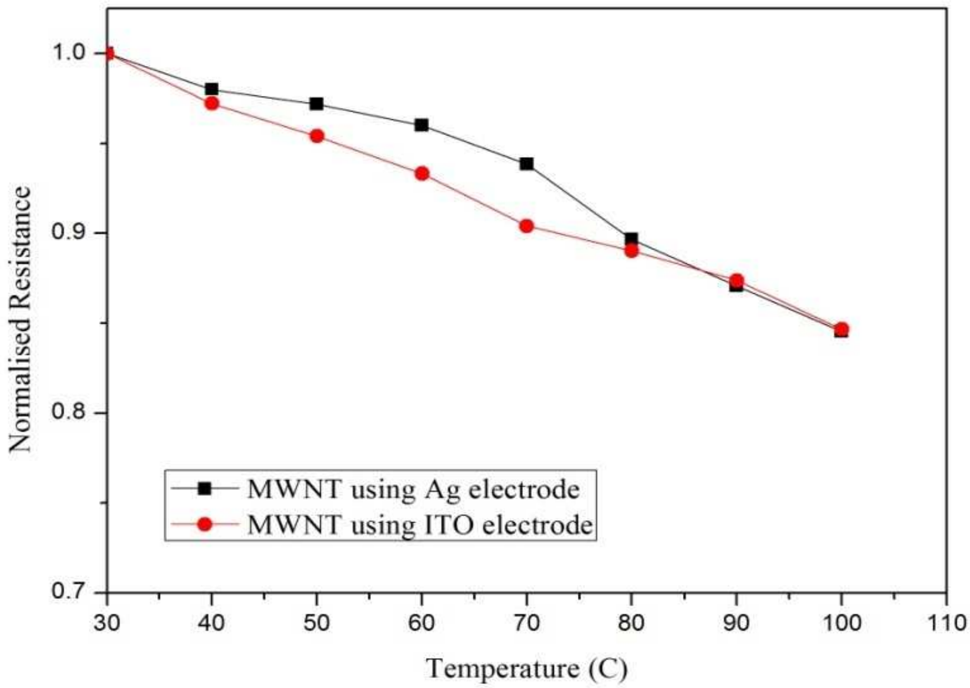

Figure 15 Effect of electrode

5.1.7 Quantitative Evaluation of the Sensor

There are mainly two parameters that require consideration in this section and these include:

5.1.7.1 Sensitivity

The sensitivity of the sensor is defined as the slope of the output characteristic curve (DY/DX) or, more generally, the minimum input of physical parameter that will create a detectable output change. This value was found to be of about 0.3 $\%/^{o}C$ for screen printed silver, interdigitated electrode pattern on PET substrate with MWNT as the temperature sensitive material. This value was compared with commercial sensors in Chapter (3) and was found to be remarkably lower by about 70%, but when compared with one of the best sensors still in research it was found to be reasonable with a difference of about 20%.

5.1.7.2 Linearity

The linearity of the transducer is an expression of the extent to which the actual measured curve of a sensor departs from the ideal curve. There are several ways to interpret and represent the linearity of a transducer and those most widely used are: end point linearity, best fit straight line and finally least squares best fit straight line.

The one chosen in this case is the first of these techniques which is end point linearity. Usually the point that deviates most from the simple straight line will be used to specify the linearity of the transducer. The equation used for this calculation is as given below:

$$\%\mathbf{FS\ non-linearity} = \frac{\mathbf{dv \times 100\%}}{\mathbf{Vfs}} \tag{5-1}$$

This value was calculated for the same sample as the one mentioned in the sensitivity section and was found to be 15%FS. This value was found to be reasonable even when compared to commercial sensors.

5.1.8 Quantitative Evaluation of the Sensor

In this section, several parameters are considered qualitatively and with the support of graphs. The first of these parameters is repeatability, which is a parameter that normally refers to repeatable readings from same sensor at different times, however in this case it refers to repeatability of method of manufacture of the sensor. As for aging then it refers to characteristic variation when sensor is tested repeatedly over a number of days. Finally, stability in this case refers to resistance value variation when the temperature is kept constant at 30°C and then also at 90°C.

5.1.8.1 Repeatability

In this section, repeatability stands for consistency of method of manufacture. This refers, in this case, to uniformity of the CNT layer which in this case is of MWNT nature, since the electrode pattern used was manufactured with great accuracy using vacuum techniques. Fig. 16 below shows the results obtained when samples were manufactured independently at two different occasions. They show less than 10 % variation between the two which may include variation in the heating equipment used for testing (i.e. hot chuck).

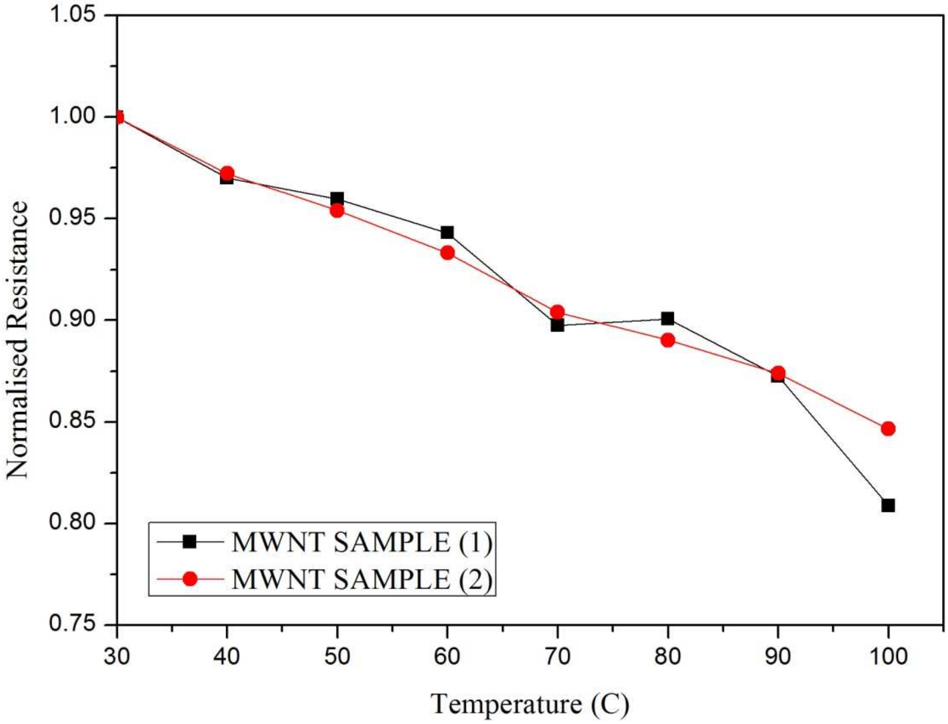

Figure 16 Repeatability

5.1.8.2 Aging

In this section, aging refers to testing the same sample on separate occasions over a period of about 9 months. Fig. 17 shows the results of this test showing that there is a maximum variation of about 6% which may yet again refer to a variation within the heating equipment used in this test.

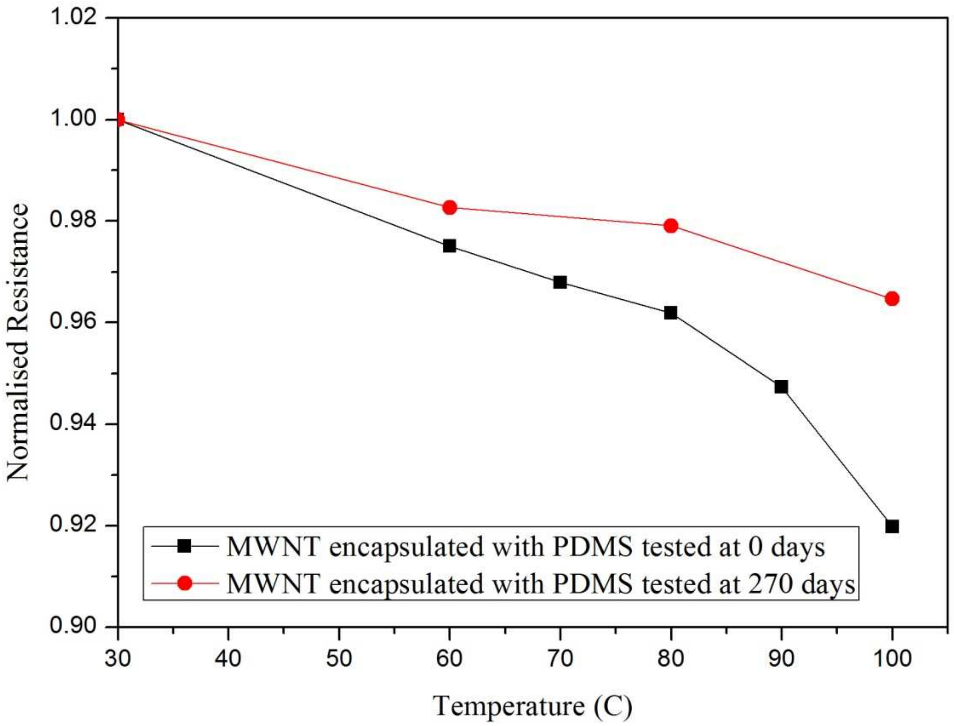

Figure 17 Aging a sample for about 9 months

5.1.8.3 Stability

In this section, as was explained above, the temperature is kept constant at two different temperatures of 30°C and 90°C. It is obvious from Fig. 18 below that the variation in the value of the resistance increases as temperature increases, which again refers to contribution of O_2 to the experiment. In the case of the test at 30°C then the variation of resistance value reduced over about 50 mins by about 1.6% whist the test at 90°C revealed a variation of resistance value of about 5%, which is far greater.

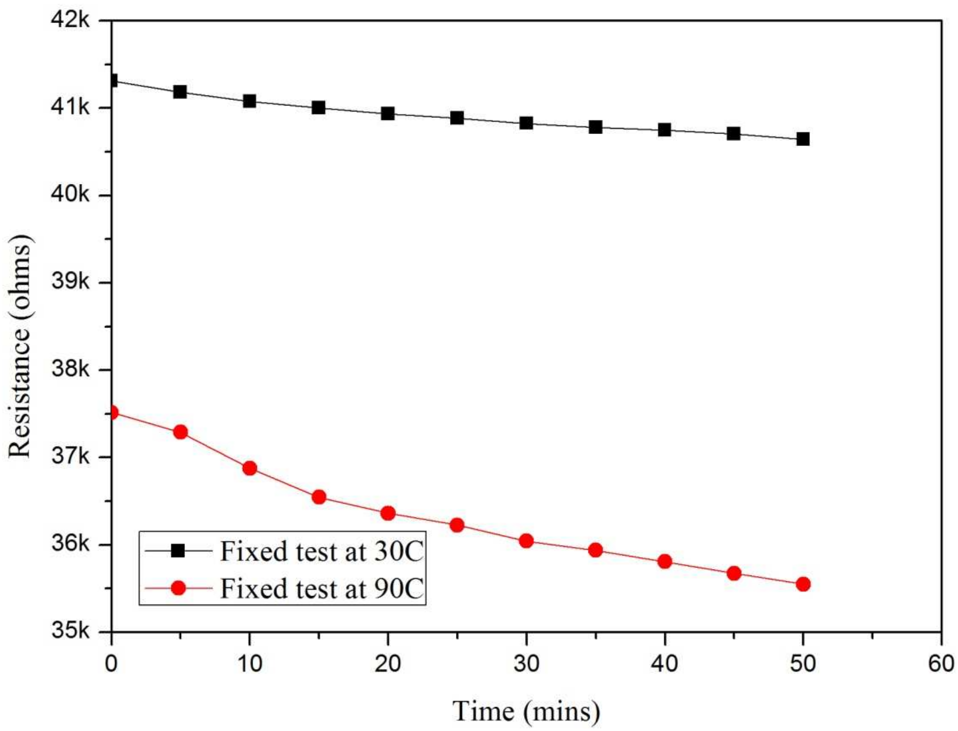

Figure 18 Fixed temperature test

5.2 Array of Sensors Investigation

This section includes two designs, one of which used spin coated MWNT as the temperature sensitive material whilst the other used inkjet printed SWNT.

5.2.1 Spin Coated MWNT array of devices

When considering the array of devices then the first thing to notice from Fig. 19(b) is that uniformity appears to be poor which, led to Fig. 19(a) being necessary in showing the nodes that show reasonable resistance versus temperature characteristics. However from Fig. 19(c) the error margin appears to be large, it can in fact reach about 40^{o}C.

The lack of uniformity occurred due to the method of CNT ink deposition being spin coating for a large 4cm x 4cm substrate.

Another technique for deposition is being considered, namely, inkjet printing. This method, however, also suffers from uniformity problems resulting from clogging and smudging. These issues are addressed and attempts are being made to produce a workable array of devices.

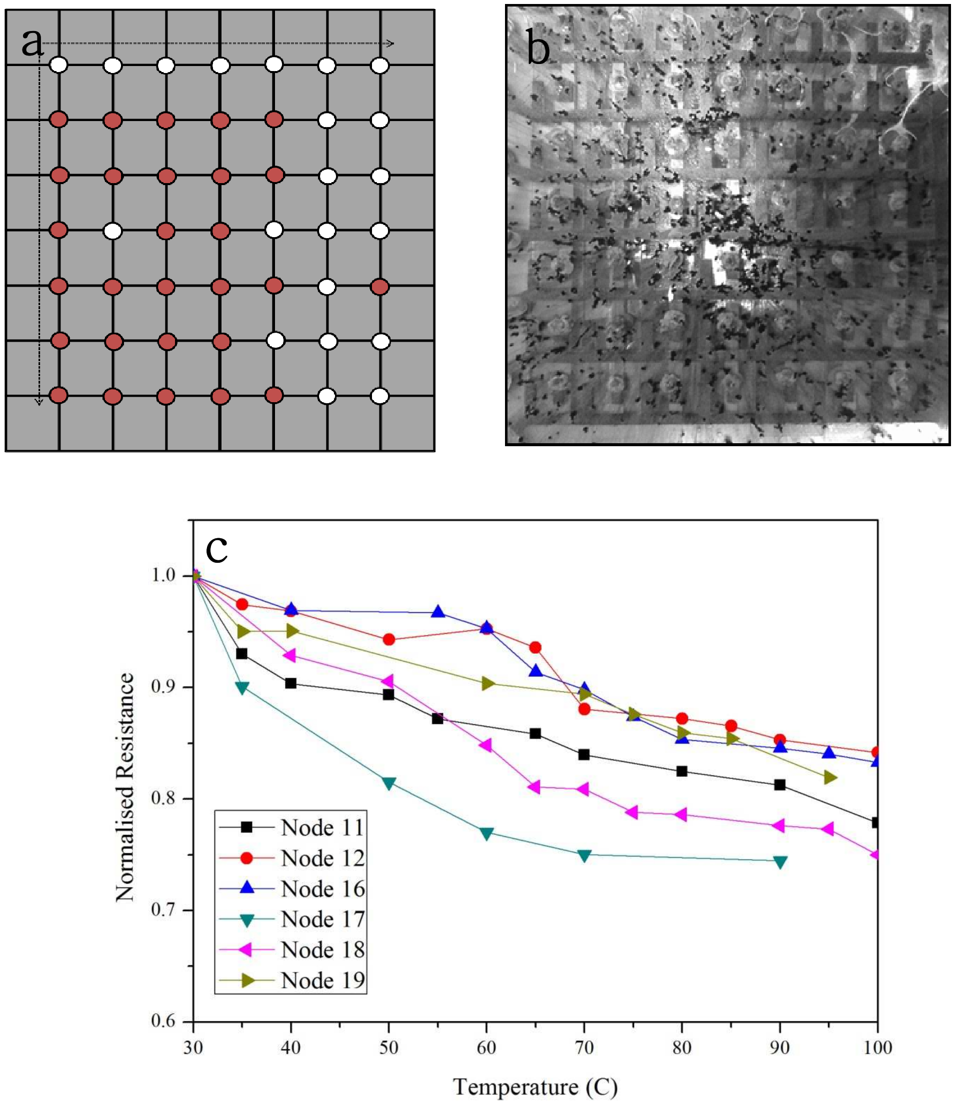

Figure 19 Array examination (a) schematic view of the array with red dots representing working nodes (b) a real view of the sensor (c) graph showing characteristics for 6 nodes

5.2.2 Inkjet printed SWNT array of devices

When considering the array of devices then the first thing to notice from Fig. 20(a) is that uniformity and transparency have improved across the whole area, which ultimately led to all nodes operating effectively. Fig. 20(b) shows the characteristics for 4 nodes which showed the best results.

The improved uniformity was achieved by changing the method of CNT ink deposition from spin coating to inkjet printing, which was necessary for a large 4cm x 4cm substrate. As for transparency, then improvement was achieved by using SWNT [from Hanwha Nanotech] which showed pure semiconducting characteristics within the temperature range of interest of (30 – 100)^{o}C.

Many other improvements can be achieved if this sensor can be commercialized, by perfecting the size of the vias, which from Fig. 20(a) appear not be as uniform as desired. Also improvements can be achieved by altering the dimensions to achieve better sensitivity, linearity as well as resolution.

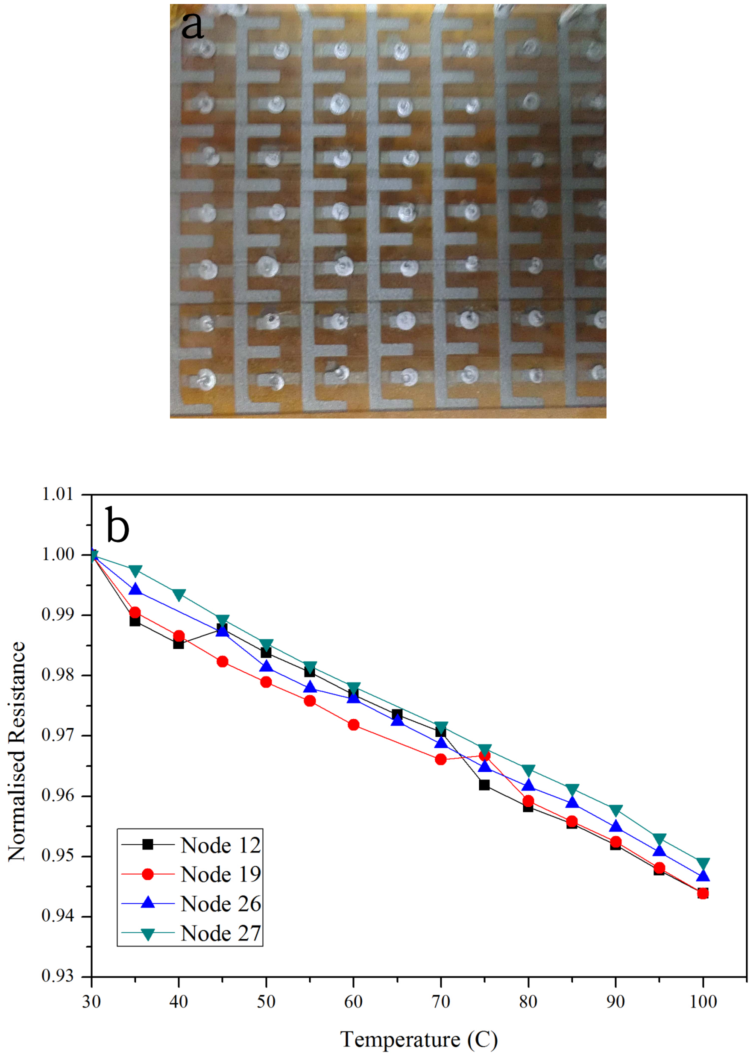

Figure 20 Array examination (a) a real view of the sensor (b) graph showing characteristics for 4 nodes

5.2.3 Problems encountered with different sensor array designs

There were many problems occurring at almost every stage of design and manufacture of the arrays, these will be stated as bullet points below.

* Design errors

  Fig. 21 and Fig. 22 below show the different designs that were considered and an explanation for their failures. Fig. 23 below shows the final design that was tested and the results of which were given in the previous section.

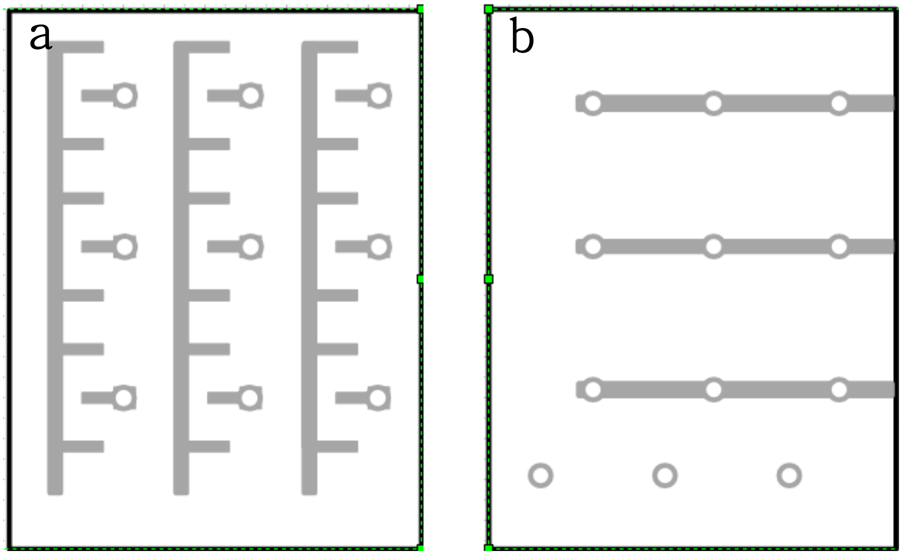

Figure 21 First design for a 3x3 array (a) top (b) bottom

This design suffered from a number of problems summarized below:

1. Alignment problems due to the small size of the sensor array.
2. Connectivity problems due to small points and small area for manoeuvre.
3. Via connectivity problems again due to small spacing between devices.
4. Connectivity problems due to screen printed electrode width of 0.3 mm is insufficient and appeared to contain many holes.

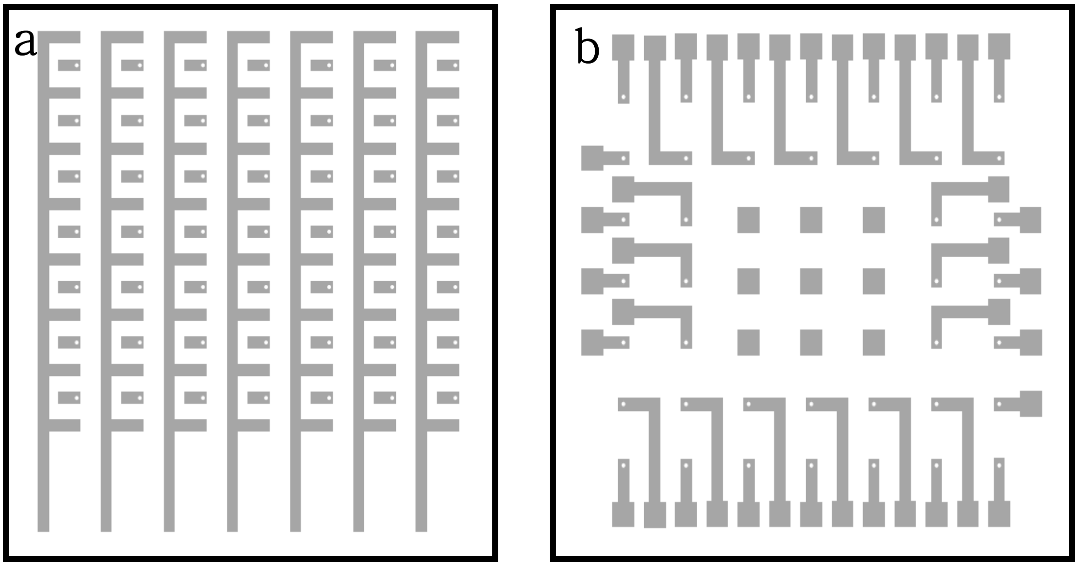

Figure 22 Second design for a 7x7 array (a) top (b) bottom

The design in Fig. 22 suffered from a number of problems summarized below, which were mostly resolved in the final design shown in Fig. 23 below.

1. Alignment problems increased since the points of contact increased.
2. Connectivity problems due to small points and small area for manoeuvre as well as increased number of vias.
3. Connectivity problems due to the increased number of wires that needed to be handled.

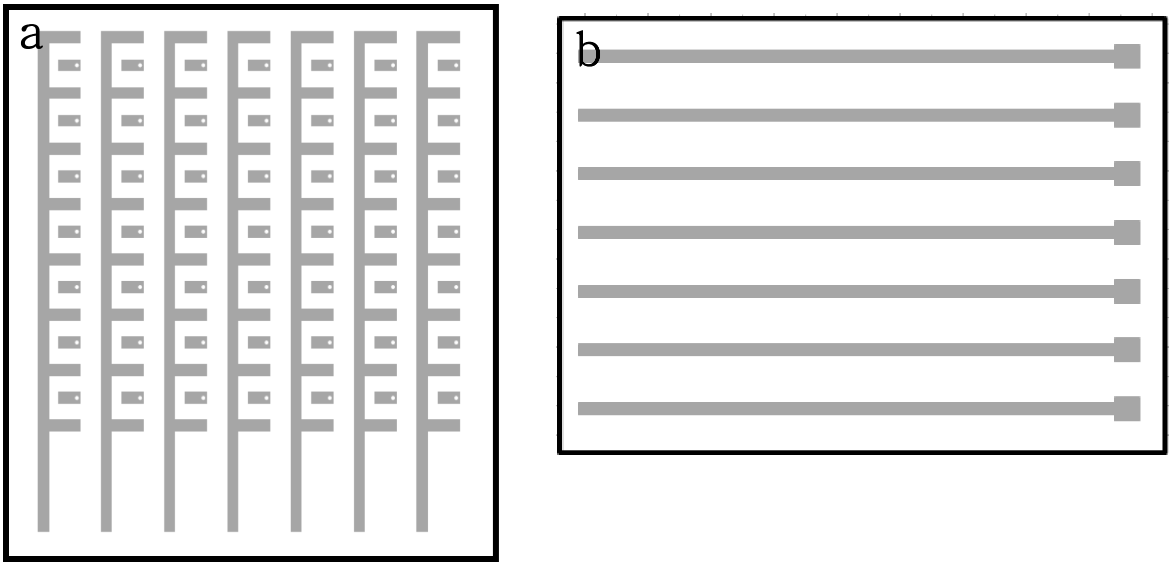

Figure 23 Final design for a 7x7 array (a) top (b) bottom

* Problem with electrode thickness

  It was found from testing sensors with electrode thickness of about 0.3 mm to be lacking repeatability due to inaccuracies in inkjet printing or inconsistencies with screen printing. It was also found that the sensor would not give readings for whole range of (30 – 100)^{o}C but in fact it shows signs of open-circuiting after about 70^{o}C which may be due to electromigration effects.

* Problem with electrode separation

  Different electrode separation distances were used in the experiments and it was clearly found that the CNT resistance change with temperature was only accurate if the separation was at a minimum of about 0.8 mm. This may be again due to problems with limitations with printing accuracy. This is the reason for choosing a separation distance of about 1 mm for final design to ensure that the sensor behaviour is as to be expected from the graphs obtained before in this thesis.

* Problems with electrode pattern being inkjet printed

  There were problems inkjet printing due to a change in the silver ink which meant that settings of the inkjet printer needed to be modified, something which took a very long time and so screen printing was chosen as an alternative method, one of which is reliable providing that thickness of line is around 1 mm. Screen printing also avoids any waste of materials (i.e. substrates) which may be caused by clogging of the heads with ink which causes certain areas of the pattern not to be printed correctly or not at all.

* Problems with making vias for double layer array design

  There were two methods used to make holes for the double layer array, which include:

1. Using needle

   The reason for using a sharp needle at beginning is due to lack of a stand for drill and so it was thought to give better control. However a problem occurred and the substrate cracked due to needle getting stuck. It was also impossible to create holes for double layer at same time due to lack of force that can be applied through the needle which created alignment problems later in the manufacturing process.

2. Using drill

   Despite the fact that there was no specialised stand for the drill available in the laboratory, it was deemed to be the best method for creating vias, especially given that double layer could be achieved at same time with silver ink applied straight after which improved the connectivity greatly. There were difficulties to create holes using the drill without the stand and there were a few errors in alignment.

Chapter 6

Conclusions

Adsorbates play a big role in circuitry/sensory devices that make use of CNT. This is since they can play a big role in influencing electric fields near the CNT. These adsorbates may well be in the form of ions of water vapor on the surface of the device. The effect of these adsorbates was examined in more detail as two sensors with two types of inks were examined (SWNT and MWNT) not only in an atmospheric environment but also in Argon and high vacuum environments. The temperature versus resistance characteristics showed different levels of change for MWNT and SWNT, whereby, SWNT was the most affected by the environmental change. This may be due to the inherent metallic nature of the SWNT behaving as a semiconductor only due to adsorbates. On the other hand, MWNT appears to behave as a semiconductor in all the different environments showing a minor reduction in resistance only within a high vacuum environment.

Another factor that may play a role is the surface roughness of the sample. It was found when the topography of the samples was considered that the MWNT surface is rougher than the SWNT surface. This could have led to adsorbates being trapped within the rougher surface causing the semiconducting behaviour.

From all the tests carried out so far it was found that the MWNT ink gave the best results for the application of a temperature sensor. A decision was also reached that the substrate to be used was PET due to its flexibility as well as transparency. Moreover, PDMS was also found to be necessary for encapsulation of the sensor to protect it from environmental effects. Finally, it was found that screen printing was the best technique to obtain a workable electrode pattern.

As for the array of devices then it was found after testing that spin coating was not an efficient technique for its large area. This is the reason for considering at this late stage, inkjet printing which led to an array of devices with much better uniformity, although much reduced sensitivity, which could be attributed to ineffective via formation as well as PDMS encapsulation techniques.

Chapter 7

Conference and Journal Publications

Conference Paper

F. A-Naimi, S. Kim, Y. Park, J. Byun, H. Song, and Y. Hong*, "Temperature Sensor Devices Based on Carbon Nanotubes Ink", IMID, Daegu, Korea, August 2012 (accepted oral)

Journal Paper

F. A-Naimi, S. Kim, J. Byun, **T. Kim, S. B. Ji**, and Y. Hong*, "Flexible CNT Based Temperature Sensor Array" (in preparation)

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국문 초록

최근 로봇과 인공 의족이 필요성이 증가되면서 이러한 것들이 느낄 있도록 하는 것에 대한 필요성 또한 증가되고 있다. 그 결과 로봇이 실제와 같은 반응이 가능하게 되고 또한 인공 의족의 사용자가 그들이 잃었던 감각을 회복할 수 있게 되어 일상적인 생활이 가능하게 될 것이다.

지금까지 많은 연구 그룹들이 압력 센서와 온도 센서에 관심을 가져왔고, 이 논문에서는 온도 센서에 대해 다루었다. 이 논문에서의 온도 범위는 30 - 100 ℃ 이고, 온도 감지를 위해 사용된 물질은 carbon nanotube (CNT)로 지난 수 십년 간 많은 관심을 받았다. CNT ink 에는 multiwall CNT (MWNT) 와 single wall CNT (SWNT) 두 종류의 ink 가 있다. 이 두 종류의 ink 는 다른 환경의 조건에서 그들의 온도센서로써 적합한지 확인하기 위해 검증하였고 특성화하였다.

그 결과 MWNT 가 주어진 환경에서 저항이 온도에 비례하는 선형적인 특성을 보여, 온도 센서에 적합함을 확인할 수 있었다. 이를 위해 spin coat 된 MWNT 층과 screen print 된 silver 전극 패턴을 이용하여 온도 센서 소자를 제작하였고 이를 통하여 0.3%/ ℃ 의 sensitivity 와 15%FS 의 선형성을 얻을 수 있었다.

또한 우리는 위와 같이 MWNT ink 를 이용한 단일 소자를 기반으로 센서 어레이를 만들려고 시도하였다. 그러나 단일 소자를 만들기 위한 MWNT 의

spin coating 방법은 소자의 균일성이 떨어지기 때문에 센서 어레이를 만드는 데는 적합하지 않았다. 따라서 이를 위해 대체 방법인 inkjet printing 방법이 고려되었다. 그 결과, 센서 어레이는 보다 나은 균일성을 보였지만 sensitivity 특성은 조금 감소하였는데 이는 비효율적인 PDMS encapsulation 기술과 via 형성 때문일 것으로 생각된다.

주요어 : 탄소 나노튜브, Singlewalled/Multiwalled 탄소 나노튜브, 온도센서, 어레이 소자

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