Flexible Transparent Conductor Film using Graphene-Carbon Nanotubes on PDMS

by

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14619

Dissertation submitted in partial fulfilment of
the requirements for the
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CERTIFICATION OF APPROVAL

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Approved by,

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(Dr. Mohamed Shuaib B Mohamed Saheed)

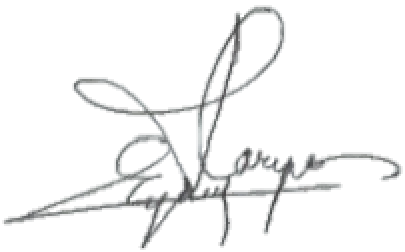
UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2016

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



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MARI PAZ EYANG MBA OBAMA

ABSTRACT

Conventional transparent conductive films (TCF) used indium tin oxide (ITO) as the conductive material but the issues with film brittleness, low infrared transmittance, scarcity of indium, and high-cost of the preparation procedure limits the mass production of flexible TCF. Carbon nanotube (CNT) and graphene are two promising alternatives to replace ITO-based TCF due to its high electrical conductivity, excellent mechanical strength, flexibility and transparency, and optical properties. Graphene and graphene-CNT was grown using the CVD method and characterized using the Raman spectroscopy, Hall Effect measurement system, the UV-vis spectrophotometer and the four point probe method to study the mobility, resistivity and optical properties of graphene and graphene-CNT on polydimethylsiloxane (PDMS) substrate. The average mobility obtained for graphene and graphene-CNT are 1633.76 cm^2/Vs and 3445.74 cm^2/Vs respectively. The results demonstrated that graphene-CNT sample has three times higher mobility than graphene. This is due to the incorporation of graphene and CNT which improve the conductive filler materials. Raman spectroscopy provides the layer thickness by analyzing the peak intensity ratio of 2D and G bands. And the I_{2D}/I_G ratio confirms the high quality or defect free of graphene. On the other hand, the wavelength range demonstrates that graphene and graphene-CNT UV-Vis study have 97% transmittance at >500nm due to its optical properties.

This results demonstrate that graphene-CNT on PDMS composites is a promising material for future applications.

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I am also grateful to UTP Post Graduate students working in Nanotechnology Lab, Mr. Kang Chun Hong, Ms. Summaira Abbasi and Mr. Mohamed Salleh B Mohamed for their time spend in helping me by sharing their knowledge, advising and teaching me how to operate an equipment.

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ABBREVIATIONS AND NOMENCLATURES

FYP: Final Year Project

CNT: Carbon Nanotube

TCF: Transparent Conductor Film

PDMS: Polydimethylsiloxane

PMMA: Poly methyl methacrylate

ITO: Indium Thin Oxide

SEM: Scanning Electron Microscopy

TEM: Transmission Electron Microscopy

CHAPTER 1

INTRODUCTION

This chapter focus on the experimental and theoretical studies on graphene and carbon nanotubes (CNTs) hybrid composite. A review and understanding of 2D graphene and its electrical properties which attracts the attention of researchers.

1.1. Background

Graphene was discovered in year 2004 and is a promising material for electronic devices due to its zero band gaps, high electrical conductivity and carrier mobility. It is a two dimensional (2D) carbon atoms forming a hexagonal (honeycomb) lattice structure as shown in Figure 1. Aside from being extremely conductive and strong, graphene is becoming more demanded to work with due to its optical transparency. Simply because graphene is thin and photons easily pass through it.

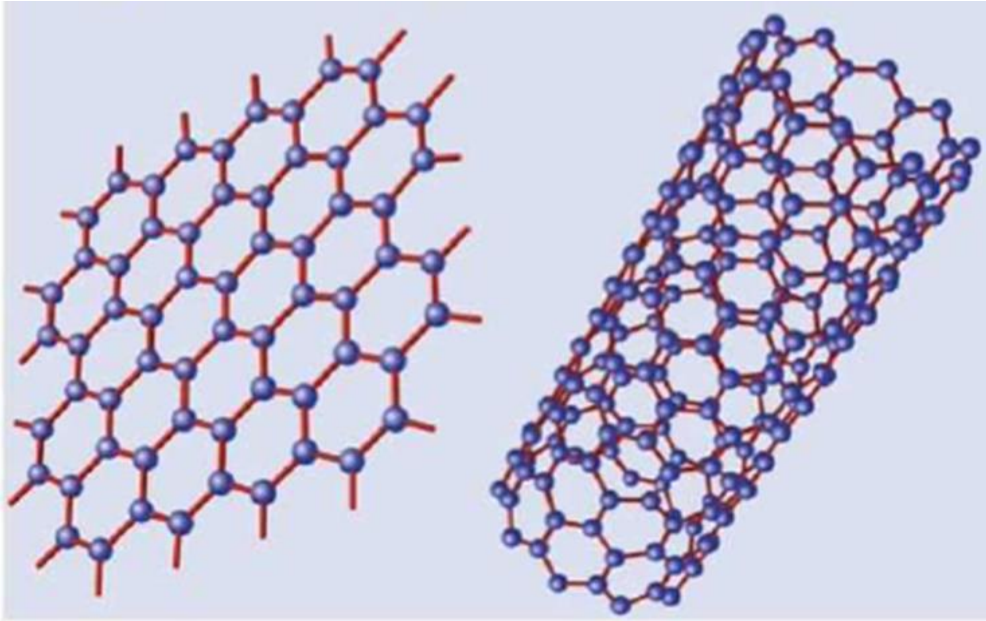

Figure 1. Graphene (Left). Carbon nanotubes (Right). Adapted from Ref. [1].

Graphene is nearly transparent, it preserve its 2D structure at room temperature and it also has its several properties similar to CNT. Graphene is stronger than steel, very stretchable with higher thermal conductivity that silver.

Carbon nanotubes (CNT) on the other hand is a rolled up graphene sheet into a hollow cylinder. CNT was discovered much earlier than graphene in 1991, also been used extensively in various fields due to ease of mass production and its comparable mechanical properties to graphene. However, graphene is a better nano-filler than CNT in certain aspects such as thermal and electrical conductivity [2]. For electronics, biotechnology, medicine and other applications, it is important to synthesis CNT that exhibit the desired physical properties, form the desired pattern, made low-resistance contact with electrodes, etc. [3].

Technology nowadays is dominated by touch related applications such as hand phones or PC and curved devices as TVs or hand phones. More flexible products are being used daily. A flexible transparent conductive film (TCF) is a new type of material with good properties and characteristics. It is an alternative to indium thin oxide (ITO) which do not possess such characteristics and it is expensive and brittle. Therefore a lot of researchers are focusing on finding a new flexible transparent film (TCF); and carbon derived materials are an alternative due to its high mobility, low light absorption and flexibility. Fused CNT and graphene, both components truly preserve their intrinsic electrical and mechanical properties. The composite films are highly flexible, transparent and conductive [4].

1.2. Problem Statement

Presently available flexible transparent conductive films (TCF) employed indium tin oxide (ITO) but the issues with film brittleness, low infrared transmittance, scarcity of indium, and high-cost of the preparation procedure limits the mass production of flexible TCF. Graphene and CNT emerged as good candidate to replace ITO as they are mutually complementary in structure and properties such as ultrahigh mechanical strength and electrical conductivity. In this project, a flexible TCF film using graphene-CNT composite on PDMS will be developed to improve the properties of graphene on a transparent and flexible film; which will draw a great deal of attention in various fields of electronics, such as flexible optoelectronics, field effect transistors, flexible batteries, wearable devices, and implantable medical devices.

1.3. Objectives and Scope of Study

The objectives of this research is to develop flexible TCF using graphene-CNT hybrid on PDMS. The research elements undertaken in order to achieve the objective are:

- To optimize the synthesis of graphene and CNT in order to produce graphene-CNT hybrid with desired characteristics (conductivity, mobility, transparency, thickness, crystallinity) required for transparent film.
- To fabricate graphene-CNT/PDMS composite film that is flexible and transparent
- To evaluate the performance of the fabricated flexible transparent film in terms of sheet resistance, electrical conductivity, electron mobility, transmittance and absorption

The scope of work consists of two stages:

- The first stage will involve in integration of graphene-CNT/PDMS into a TCF. In this stage, synthesis of graphene and CNT will be performed and subsequently characterized to understand its properties. The transfer method of graphene-CNT to PDMS will be studied in order to achieve the good adhesion between the graphene-CNT and PDMS.
- Second stage will be the evaluation of fabricated graphene-CNT/PDMS TCF. In this stage, the characteristics of the TCF will be studied extensively.

CHAPTER 2

LITERATURE REVIEW

Graphene and carbon nanotubes composites are attracting researches and many studies are being carried out exploring its possible application and characteristics, as its 2D, hexagonal structure, good electrical properties makes it a potential candidate to replace the currently used ITO.

Graphene possess properties which makes it interesting for electronic applications. It is a thin conductor, transparent and flexible film that makes it a promising material.

Carbon is the fundamental atoms for life on the planet and the basis of all organic chemistry [1]. Graphene is made of carbon arrange in a hexagonal structure with exceptional physical properties such as high electrical conductivity, excellent mechanical strength, and large surface area [5]. These properties are shown in the Table 1 and compared in Table 2.

Table 1. Graphene Properties

Properties	**Up to**
Mobility	100 000 $cm^2/V{\cdot}s$
Saturation velocity	5×10^7 $cm{\cdot}s\text{-}^1$
Thermal conductivity	5000 Wm^{-1} K^{-1}

Two-dimensional (2D) because of its useful properties such as low resistance, high flexibility, high mechanical stability and high transparency to visible light[6]. The atomic structure of isolated, single-layer graphene was studied by suspending sheets of graphene between bars of a metallic grid and exposing them to transmission electron microscopy (TEM)[7]. The resultant diffraction patterns as shown in Figure 14d proves the expected lattice honeycomb electron diffraction of graphene.

Comparing graphene, carbon nanotubes (CNTs) and indium thin oxide (ITO) in terms of sheet resistance, transmittance, flexibility and its drawbacks it is partially confirm that graphene and CNT have better characteristics than ITO as shown in Table 2 below.

Table 2. ITO, Graphene and CNT comparison

	ITO	**GRAPHENE CVD FILM**	**CNT**
Sheet resistance (Ω/sq.)	10-350	30-2000	200-2000
Transmittance	88	>90	82-88
Flexibility	Inferior	Good	Good
Commercial Process	High volume	Lab scale	Lab scale
Environmental effects	Good	Good	Good
Color	Slightly yellow or brown	Colorless	Colorless
Drawbacks	Brittle, expensive, degrading over time, unreliable supply	Extremely sensitive to defects and impurities	Resistance spiking at junctions of tubes

Graphene is highly demanded by the electronic and electrical devices nowadays due to its properties. As a graphene has promise in many electronic and optoelectronic device applications result, graphene is been used in combination of different composites as polydimethylsiloxane (PDMS) to create thin transparent conductors film.

2.2. Carbon Nanocomposites

Carbon nanostructures, nano-switches, nano-devices are many structures of carbon nanocomposites. Is a promising carbon-based solution for future applications attracted researchers to examine and analyze its electrical, mechanical and optoelectronic characteristics. Carbon nanotubes interest in many different fields of study with its exceptional mechanical properties and characteristics. Carbon nanotubes are demanded for electronics, biotechnology, medicine and other applications. Carbon nanotubes exhibit metallic, semi metallic and semiconducting properties depending on chirality and diameter[8].

2.3. Graphene-Carbon Nanotubes Composite

Graphene-based polymer composites show superior mechanical, thermal, gas barrier, electrical and flame retardant properties, compared to the neat polymer[2]. Is important to consider the distribution of graphene layers in the polymer to achieve higher properties.

The integration of graphene and PDMS/polymer stack could improves the mechanical stability of the transfer support for both conventional wet transfer and bubbling transfer resulting in significantly reduced number of cracks and holes in the graphene layer [9]. Silicone elastomer (PDMS) is a transparent conducting film used in many electronic devices as solar cells, touch screens, flat panel display, etc.[2]. Graphene, CNTs and PDMS are integrated to form a flexible transparent conductive film device with high properties such as mobility, conductivity, low corrosion and resistivity.

PDMS is also referred as silicones because of its properties and the group it belongs. It is used in a wide range of applications such as contact lenses and medical devices, food, lubricants and heat resistant tiles. The advantage of PDMS is its excellent transparency, good flexibility, electrical conductivity and thermal stability. That makes it to be involved in all the latest research involving nanocomposites.

Carbon nanotubes in the forms of single or multiple shells and have two major uses for flexible macro-electronics. Carbon nanotubes are discussed in many research in the last decade due to its high electrical and mechanical properties. It poses a crystal structure form by a layer of graphene rolled into tube structure. The malleable and transparent nature of the graphene-etched polymer depicted in Figure 2, could potentially result in foldable displays, flexible solar panels and a number of other electronics applications[10].

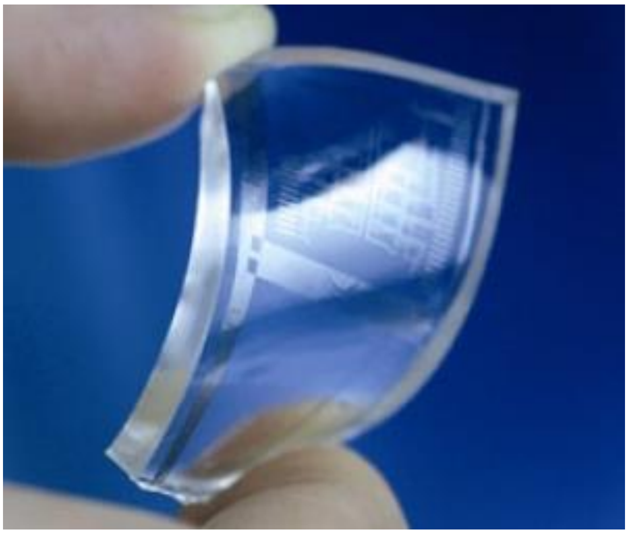

Figure 2. Stretchable graphene transferred onto a silicon-based polymer [11].

The nanotechnology revolution viability would have a huge impact on our lives, economies, countries and the society in general in the near future. Among the effects, they emphasize its potential impacts in medicine, biology, environment and technology.

Nowadays there are major practical advances already, but since the discovering of graphene by Geim and Novoselov in 2004 and despite all the advances concerning possible applications there is not yet a mass market product.

2.4. Flexible Transparent Conductor Film (TCF)

TCFs are used in many devices from liquid crystal to organic light-emitting diodes (OLEDs), solar cells and smartphone touchscreens as shown in Figure 3. Through the years, the usages of touch related materials will increase the market size in millions of dollars.

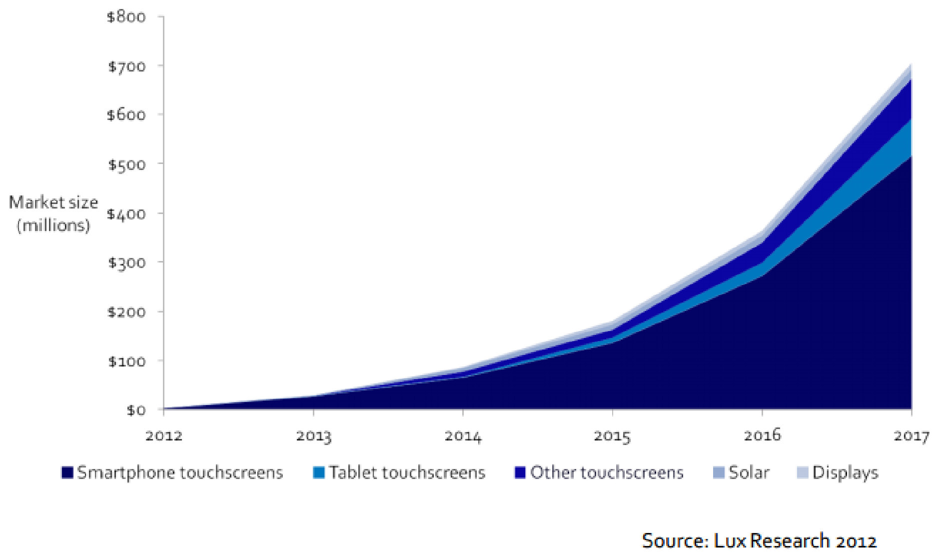

Figure 3. Market size increment through the years

Presently, the most used in such applications is indium thin oxide (ITO). A substitute is needed, graphene can be a possible replacement. Its properties are demanded by future applications and study by researchers all over the world. TCFs composite with graphene demand will increase as shown in Figure 4.

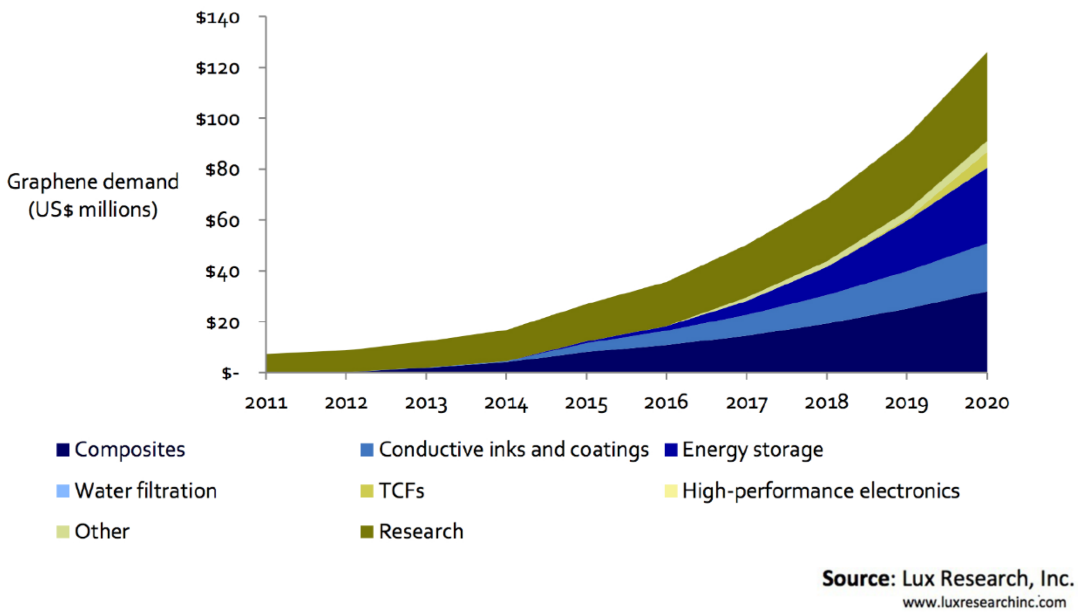

Figure 4. Graphene Demand in Future Years.

Transparent conductive films (TCFs) are extensively used in different electronic applications. This optoelectronic device coupled light and electricity together.

Chemical vapor deposition (CVD) is utilized for the growth of graphene and fabrication of TCFs due to its electrical, mechanical and optical properties. Transparent conductive materials such as conducting polymers, carbon nanotubes (CNTs), graphene, and metal nanowires have been considered as possible alternative materials for flexible TCFs[11].

Integrating graphene with CNT in a silicon base will generate a flexible transparent conductive film (TCF) having high carrier mobility, current carrying capacity and elastic property.

CHAPTER 3

METHODOLOGY

3.1. Synthesis and Characterization

This chapter focuses on the preparation, synthesis and characterization of graphene and graphene-CNT films. The growth of graphene and graphene-CNT films is performed using chemical vapor deposition (CVD) technique. Graphene and graphene-CNT films will be studied and characterized using several analytical tools, such as the Hall Effect Measurement System, UV-VIS and Four Point Probes, in order to understand its electrical, optical and material characteristics. At the end stage, graphene-CNT/PDMS composite film will be fabricated and its properties will be studied and optimized to produce good flexible TCF. Figure 5 illustrated the progress flow to obtain flexible graphene-CNT/PDMS TCF.

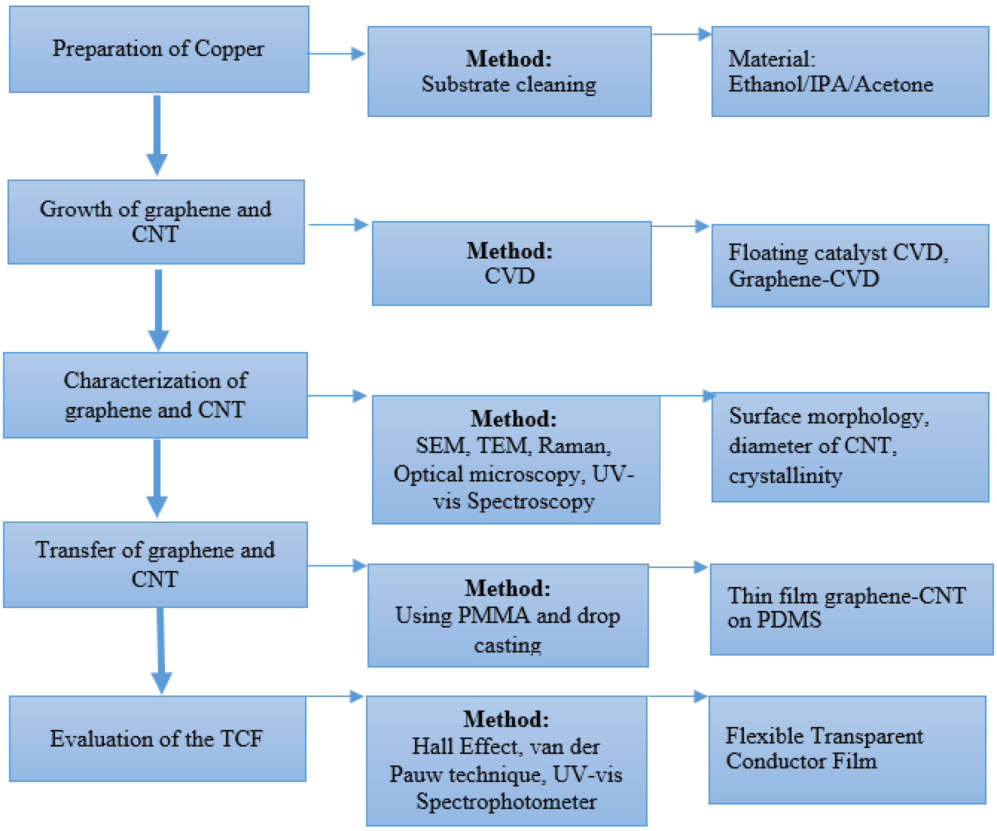

Figure 5. Process Flow to obtain Flexible Transparent Conductive Film (TCF).

3.2. Growth of Graphene and Graphene-CNT

Chemical vapor deposition (CVD) system was used to grow graphene and graphene-CNT films by using copper foil. The procedures to grow the graphene-CNT are similar with graphene and as described in the following sections.

3.2.1 Preparation of copper foil for graphene synthesis

1) Cut the copper foil into different shapes and size as needed as shown in Figure 6a. Substrates are cleaned using ethanol, acetone and IPA.

2) A quartz glass, previously used for graphene growth, was reused. The foils were placed on it and inserted into Graphene CVD system as shown in Figure 6b.

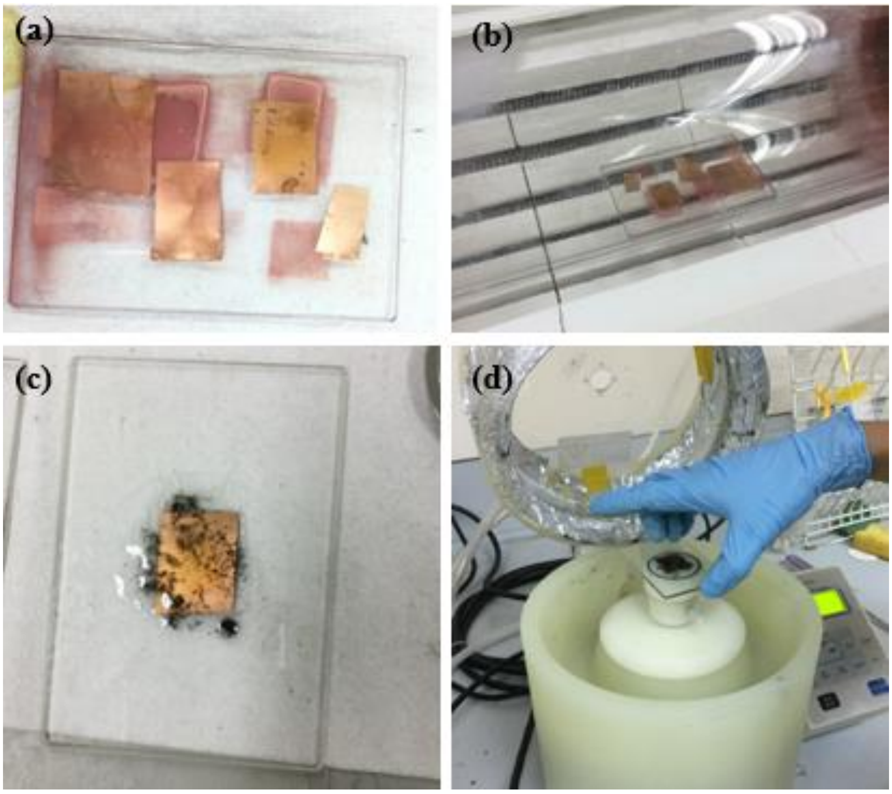

Figure 6. a) Different sizes of copper foil b) Copper foil inserted in CVD c) Dispersed CNT on a copper foil d) Dispersed CNT uniformly spin-coated on copper foil using the spin coater.

3.2.2 Preparation of copper foil for graphene-CNT synthesis

In order to prepare copper foil for graphene-CNT synthesis, similar cleaning procedures were performed. However, before inserting the samples into CVD system, the following steps are performed:

1) CNT dispersed solution is dropped on top of the copper foil as shown in Figure 6c.

2) To obtain uniform CNT coating, sample was spin coated for 30 seconds at 3000 RPM, as shown in Figure 6d.

3.2.3 Synthesis of graphene and graphene-CNT films

Both samples were inserted onto the Graphene CVD system on quartz glass to grow graphene and graphene-CNT film, as shown in Figure 6b. Graphene and graphene-CNT were grown separately to avoid contamination on the samples.

Recipe used to grow the graphene and graphene-CNT is as shown in Table 3, which have a total of six steps. The total time to grow the graphene and graphene-CNT was 2 hours and 45 minutes.

Table 3. Graphene growth recipe

NO	Time(min)	Heater	H2(100sccm)	CH4(200sccm)	Ar(1,000sccm)	Baratron
1	40	1000	40	0	300	B
2	5	1000	40	0	300	B
3	20	1000	80	80	200	B
4	30	0	40	0	200	B
5	30	0	0	0	100	Open

Upon completion of synthesis process, the synthesized samples of graphene and graphene-CNT are as shown in Figure 7a. Samples with carbon nanotubes are easy to identify due to the blacks points on the graphene samples.

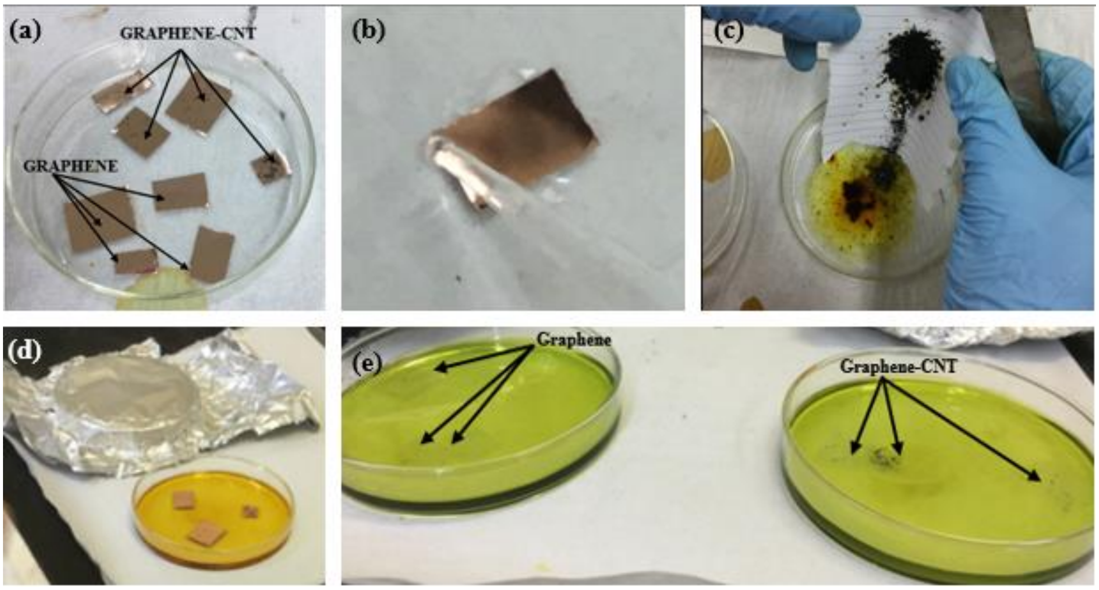

Figure 7. a) Graphene and graphene-CNT samples synthesized b) Graphene drop-coated with 4.5% of PMMA c) Preparation of the etching solution with Iron (III) chloride and distillated water d) Graphene samples on the etching solution e) Copper Foil Etched Away of Graphene and Graphene-CNT Samples

3.2.4. Transfer process of graphene and graphene-CNT

To obtain the transparent film, the synthesized samples were transferred via the following process:

1) In order to support the thin film layer during wet-etching of copper foil, graphene and graphene-CNT samples were drop-coated with 4.5% of PMMA in Anisole. It was spin coated at 2500 RPM for 1 minute and 30 seconds as Figure 6d shows.

2) The samples were baked in the oven at 80 degrees Celsius for 15 minutes. The objective of baking the samples with PMMA was to solidify it in order to hold the graphene and graphene-CNT samples after the copper foil is etched.

3) The etching solution was prepared by adding 2 grams of Iron (III) Chloride ($FeCl_3$) and 20 mL of distillated water, as shown in Figure 7c. In order to minimize cross-contamination, two separate solutions were prepared for graphene and graphene-CNT.

4) The samples were inserted into the etching solution and covered with aluminum foil, as shown in Figure 7d, to avoid contamination of solutions and samples. The solution was left for about 4 hours until copper foil was completely etched away.

5) Figure 7e shows the result obtained after 4 hours, where the copper has been etched away from the samples.

6) To prepare the samples for different characterization, such as Hall Effect Measurement, UV-VIS, Four Point Probes and TEM, the samples were scooped out using different sample holders/substrates as shown in Figure 8a-c.

7) Before removing the PMMA, another layer of 1.4% of PMMA in Anisole was spin-coated onto the samples as shown in Figure 8d, at 2500 RPM for 30 seconds.

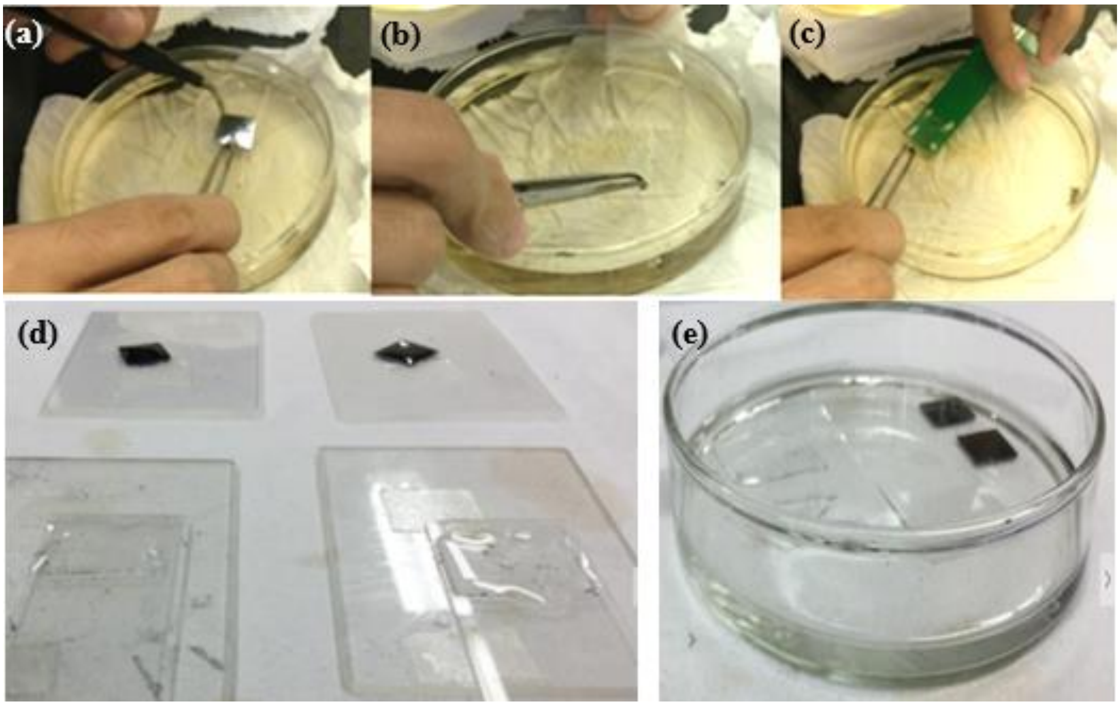

Figure 8. a) SiO_2 sample holder b) Quartz glass sample holder c) PCB sample holder d) Graphene and graphene-CNT samples with 1.4% of PMMA in anisole spin coated e) Samples on acetone solution for 2 hours.

The samples was then exposed for 30 minutes to obtain a diffused layer. After that, the samples were inserted into acetone solution and covered for 2 hours, as shown in Figure 8e. The samples were then cleaned with distilled water and dried.

3.3. Characterization of Graphene and Graphene-CNT

Graphene and graphene-CNT samples were characterized through several analytical tools and techniques, to study its properties such as resistivity, conductivity, mobility, using the Hall Effect Measurement System and UV-vis Spectrophotometer apart from that, the following equipment were also employed to complete the analytical process as the Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Raman Spectroscopy.

The mobility was studied using the Hall Effect Measurement System shown in Figure 9a. The system allows to make automatic measurement of resistivity and mobility in a wide range of samples. A total of ten sets of data were collected for graphene and graphene-CNT samples.

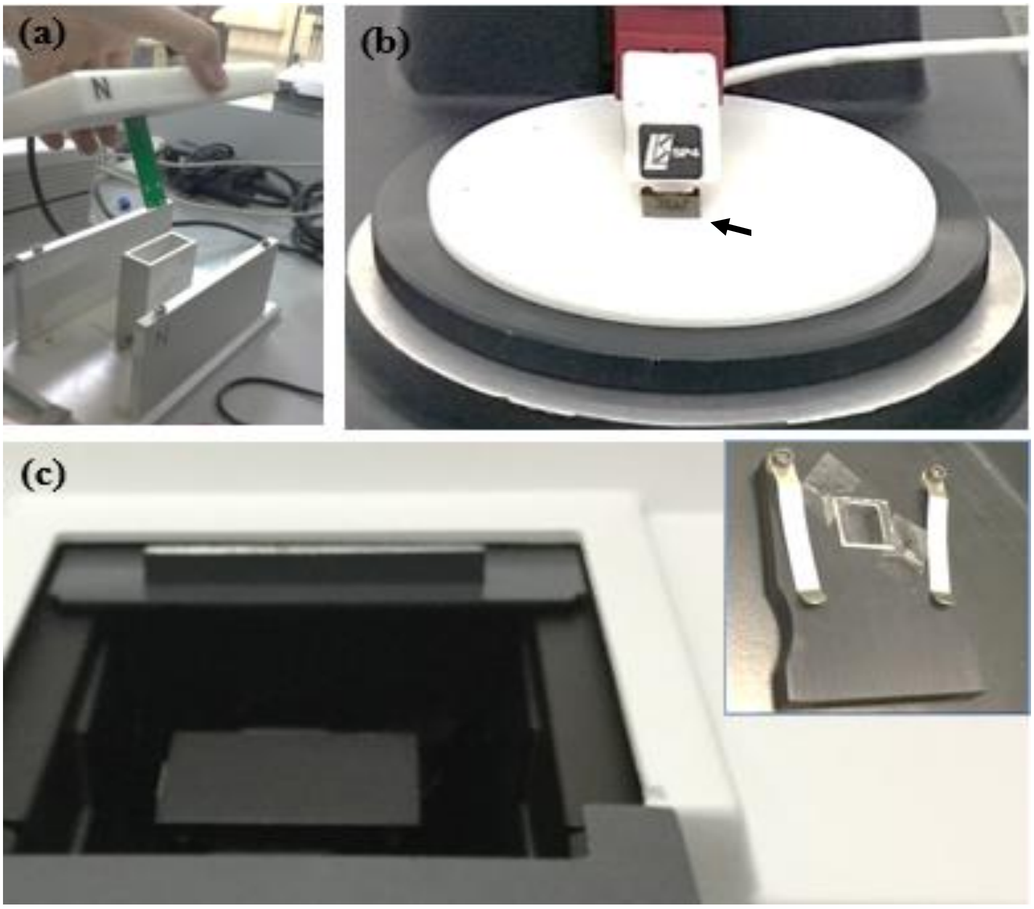

Figure 9. a) Hall effect measurement system testing graphene sample on the PCB holder b) Four point probe testing with graphene on SiO_2 substrate c) UV-VIS testing equipment. Inset image shows the UV-VIS holder holding graphene on PDMS sample.

Four Point Probe method was used to study the sheet resistance of graphene and graphene-CNT samples. Ten data were collected and analyzed. SiO2 substrate was used as the non-conductive surface as shown in Figure 9b.

The Ultraviolet-Visible (UV-Vis) spectrophotometer measured and studied the light transmittance of the graphene and graphene-CNT samples from ultraviolet wavelength to visible wavelength region. As shown in Figure 9c graphene on PDMS sample were introduced into the equipment using the holder as shown in the figure.

3.4. Transfer of Graphene and Graphene-CNT on PDMS and Evaluation of Flexible TCF

To cure the PDMS as shown in Figure 10b-f, a silicone mixture was prepared as shown in Figure 10a using silicone elastomer curing base and curing agent in 10:1 ratio respectively. The mixture was stirred about 15 minutes and leave to repose for 1 hour. The objective was to remove the bubbles on the mixture. The mixture was poured into the molds of two different sizes 1.5x1.5x0.1cm and 8x1x0.4cm previously designed and cured at 80 degrees Celsius for 1 hour and 30 minutes. Special attention was taken when pouring the mixture to avoid bubbles as it can affect the resultant material.

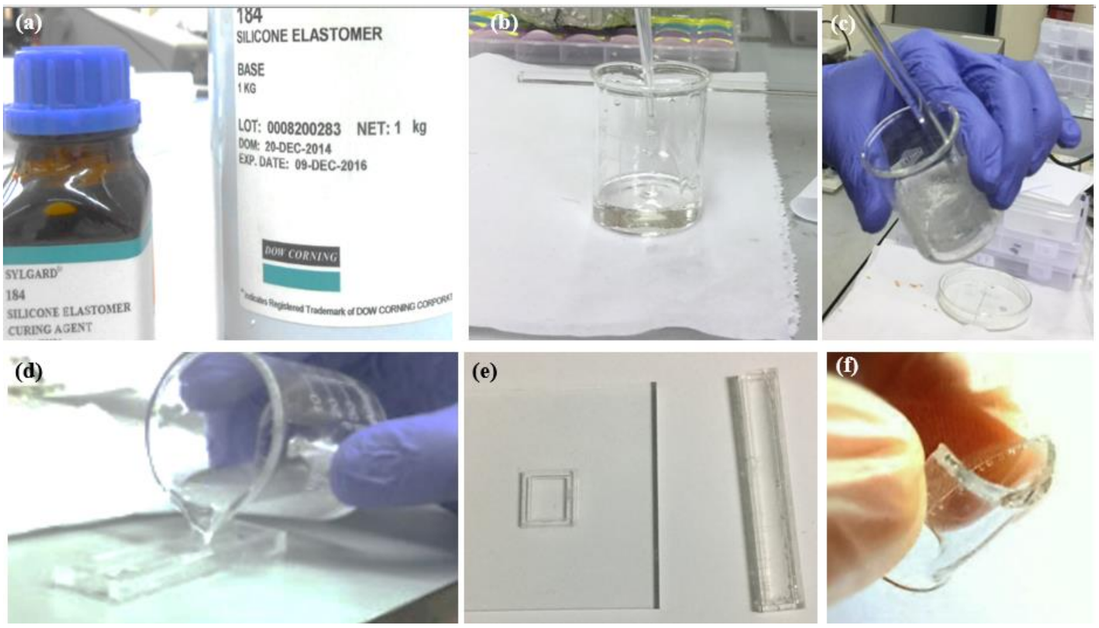

Figure 10. a) Silicone elastomer base and silicone elastomer curing agent. b) Mixture made of 10:1 ratio of base and curing agent respectively c) Stirring the mixture for 15 minutes. d) Pour the mixture into the mold e) Designed molds of 1.5x1.5x0.1 cm and 8x1x0.4 cm f) Resultant flexible and transparent PDMS.

Graphene and graphene-CNT samples were transfer using the PDMS as a base to scoop up the graphene and graphene-CNT while on clean water. The samples were heated for about 30 minutes at 80 degrees to dry it. The glass shown in Figure 11 was used as a holder to place the graphene-CNT on PDMS.

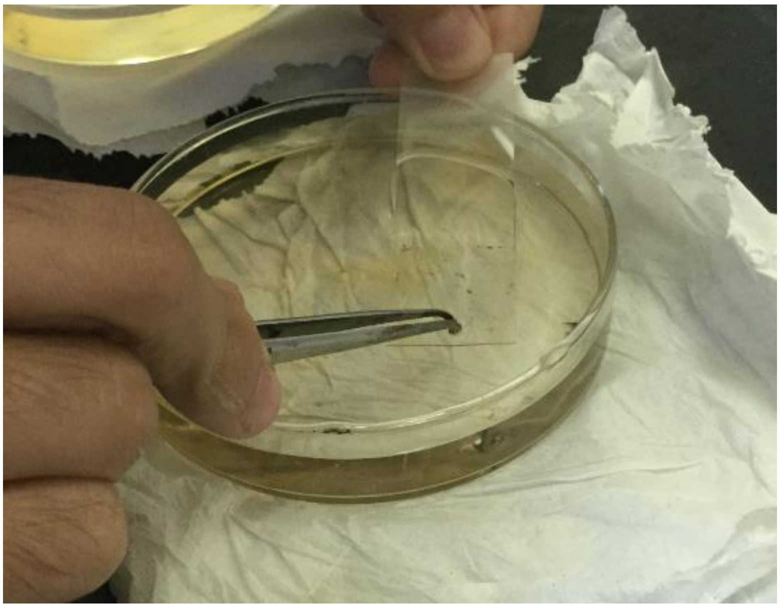

Figure 11. Graphene-CNT on PDMS.

The final obtained result was a flexible transparent film on PDMS base for graphene and graphene-CNT.

To evaluate the flexible TCF, several techniques will be used to characterize and to study the uniformity of flexible TCF, mobility, conductivity, resistivity, transmittance and absorption characteristics.

3.5. Tools and Hardware

The tools and hardware required to complete this project are specified below.

Table 4. Materials and Equipment required to complete the project.

MATERIALS AND EQUIPMENT	
CONSUMABLES	EQUIPMENTS
Copper foil	SEM & TEM
Iron (III) Chloride	Graphene CVD
PMMA	Spin Coater
Silicone Elastomer Agent	Oven
Silicone Base Agent	Hall Effect Measurement System
PDMS	UV-Vis Spectrophotometer
Anisole	Four Point Probe System
	Raman Spectroscopy
	Digital Multimeter

3.6. Milestones and Schedule

This project was feasible and was completed in the given time frame (two semesters). Table 5 and Table 6 shows all required activities and milestones that must be completed weekly to complete this project throughout the two semesters. All the materials and equipment required in this project are shown in Table 3.

During Final Year Project I, Table 5 shows all the activities that were completed and milestones that were achieved weekly. Final Year Project II, shown in Table 1, main objectives were to synthesize and characterize the flexible transparent conductive film (TCF) obtained.

Table 5. Gantt chart FYP I

ACTIVITY/ WEEK	**WEEKLY TASK / MILESTONE**													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of topic	■	■												
Understand the properties and characteristics of graphene			■	■										
Understand the properties of PDMS				■	■									
Understand the properties of CNTs					■	■								
Submit first draft of Extended Proposal					■									
Submission of Extended Proposal						◇								
Project work continues							■	■	■	■	■	■	■	■
Proposal Defense								■	◇					
Project work continue									■	■	■	■	■	■
Submission of Interim First Draft Report													◇	
Submission of Second First Draft Report														◇
Submission of Interim Report														◇
Synthesis and growth of graphene and CNT														◇

Table 6. Gantt chart FYP II

ACTIVITY/ WEEK	**WEEKLY TASK/ MILESTONE**														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Write Technical Paper	■	■	■	■	■	■	■	■	■	■	■	■			
Preparation of PDMS		■	■	■											
Characterization of graphene on PDMS						■	■	■	■						
First draft of Project Report to SV						◆									
Characterization of Graphene-CNT on PDMS							■	■	■	■					
Submit final version of Progress Report							◆								
Evaluation of the Flexible TCF									■	■	◆				
Pre-SEDEX										◆					
Submission of Draft Final Report											◆				
Submission of Dissertation (Soft bound)												◆			
Submission of Technical Paper												◆			
Viva													◆		
Submission of Project Dissertation (Hard bound)															◆

■ **Progress**

◆ **Milestones**

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Results

Graphene and graphene-CNT thin films were successfully synthesized via CVD method and subsequently characterize the flexible TCF obtained from the methodology. The recipe total time to grow the graphene was 2 hours and 45 minutes as shown in Table 3. To achieve a good quality graphene, it was important to manually move the heating chamber to the side for a fast cooling. By moving the heater, the temperature curve (purple line and green line) shown in Appendix 3-1 demonstrates that the actual temperature (green line) reduces at almost same rate as the equipment temperature (purple line). The actual time taken to grow the graphene and graphene-CNT was 1 hour and 45 minutes each.

Different testing methods had been completed with the growth samples. The objective was to study the resistivity, mobility and optical properties of the obtained samples. The samples layers structure are as shown in Figure 13. The composite film possess a layer of PDMS, then the Graphene-CNT composite growth using CVD

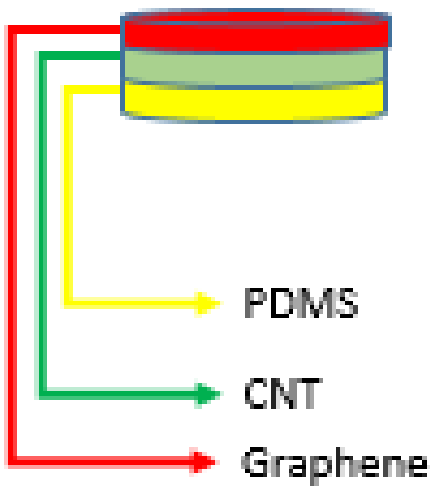

Figure 12. Composite film layer structure

4.1.1 Characterization of Graphene and Graphene-CNT using Raman, TEM and SEM

Figure 13 shows the Raman spectra obtained of the graphene sample on SiO_2 substrate. For single layer graphene the 2D band is observed to be a single symmetric peak with a full width at half maximum (FWHM) of ~ 28.50 cm^{-1}. Figure 13 proves the existence of graphene single layer by analyzing the peak intensity ratio of 2D and G gaps. G mode value corresponds to the stretching motion located at 1607.33 cm^{-1}. The peak of the spectra around 1600 cm^{-1} is G-band corresponding to the in-plane, zone-center, doubly degenerate phonon mode in graphene [12] The absence of D band shows the high quality of graphene. The peak of the spectra around 2700 cm^{-1} is 2D-band corresponding to second-order double resonant process between nonequivalent K points in the Brillouin zone of graphene, involving two zone boundary phonons[13]. It also demonstrate the existence of graphene at 2700.04 cm^{-1} and the ration I2D/IG confirm the existence of few layers of graphene and a high quality or defect free graphene sample.

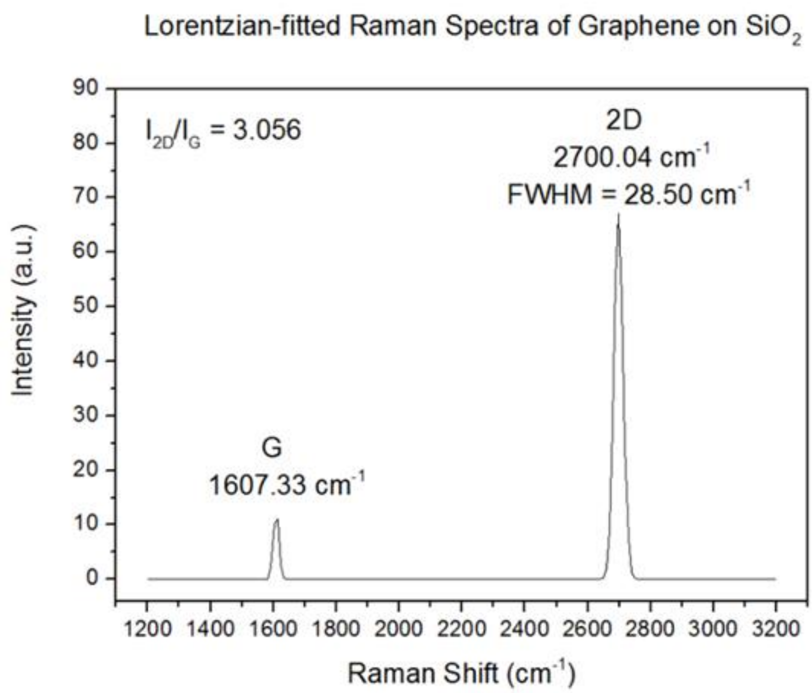

Figure 13. Raman Spectra of Graphene on SiO_2 substrate

To confirm the presence of graphene and graphene-CNT on PDMS SEM and TEM was performed as shown in Figure 14 and Figure 15.The structure of graphene-CNT composite was analyze using the transmission electron microscopy (TEM) system. Figure 14a shows TEM image of the nanotube structure in the composite analyzed where the single wall can be seen easily, while Figure 14b is a high resolution image showing the length of the CNT layer which is approximately 43.307 nm. This TEM analysis proves that graphene-CNT were well combined on the sample analyzed.

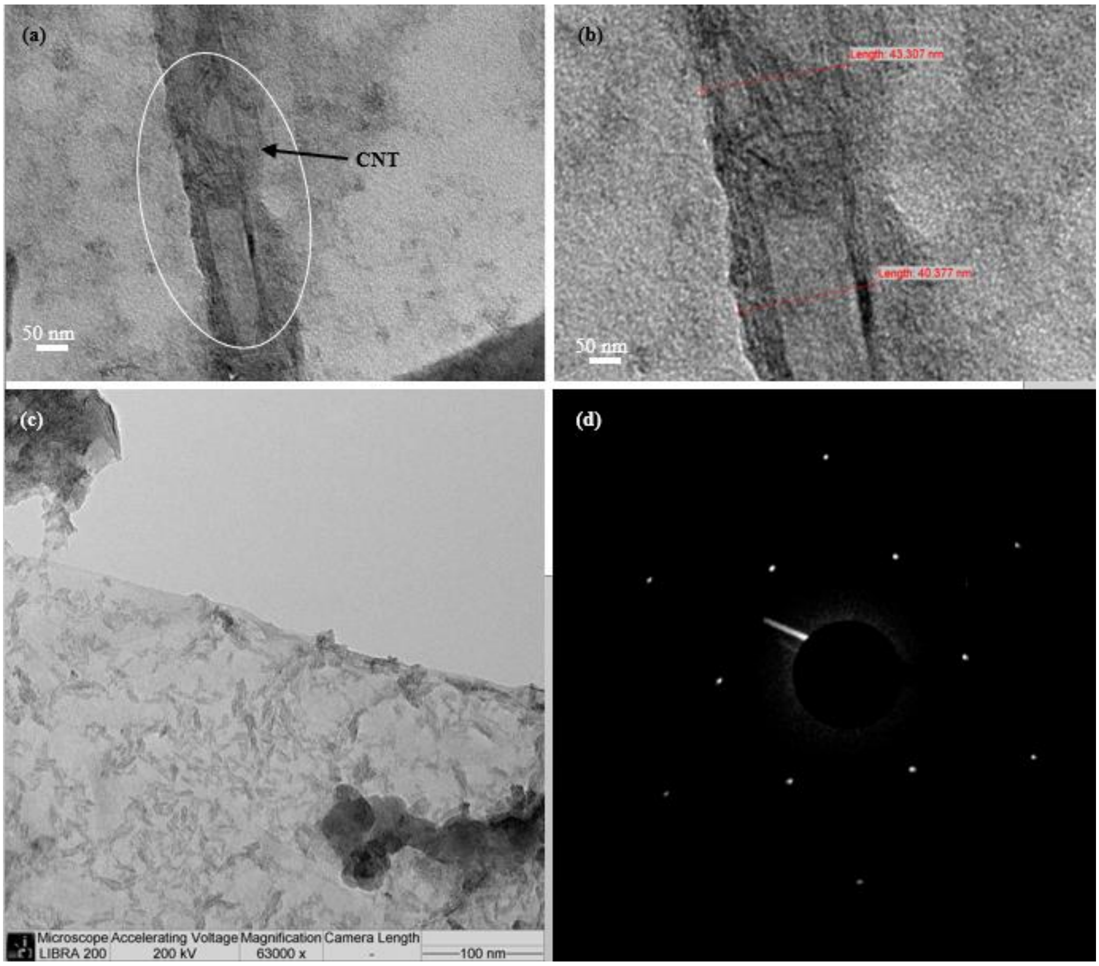

Figure 14. a) Transmission Electron Microscopy (TEM) of CNT (scale bar: 50 nm) b) TEM of CNT structure and the layer length of 47.307 nm. c) TEM image of graphene at 100nm scale bar d) Selective area electron diffraction of graphene.

TEM analysis was carried out to confirm the dispersion of graphene-CNT composite film. Graphene-CNT monolayer composite is shown in Figure 14c. To prove the existence of graphene the TEM analysis was performed obtaining graphene hexagonal structure shown in Figure 14d with a single crystalline lattice structure.

Scanning electron microscopy (SEM) was also used to analyze the composite. Thorough inspection of the graphene films using scanning electron microscopy confirmed the formation of continuous films without any visible cracks[14]. Below SEM images shows the surface morphology of the graphene-CNT composite film. Figure 15a shows a high quantity of CNT on the composite film and Figure 15b shows the uniformity of the film analyzed.

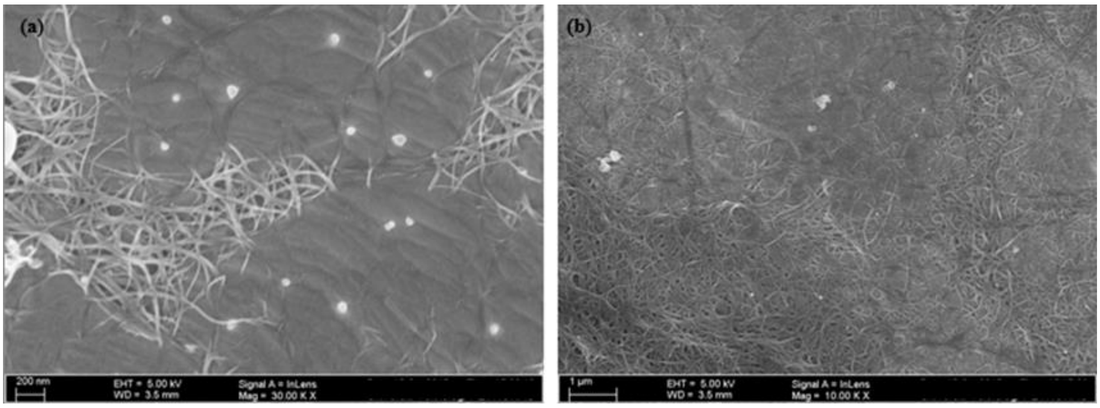

Figure 15. Scanning electron microscopy (SEM) on graphene-CNT at two different scales. a) At 200 nm scale bar. b) At 1 µm scale bar.

4.1.2 Electrical Characterization of Graphene using Hall Effect Measurement Technique, Four Point Probe and UV-VIS

The first electrical test performed was the Hall Effect test, using the Hall Effect Measurement System as shown on Figure 9a. The average mobility obtained for graphene was 1633.76 cm2/Vs and an average resistivity of 2.55x10-5 Ωcm. The graphene-CNT sample had an average mobility of 3445.74 cm2/Vs and an average resistivity of 1.28x10-5 Ωcm. The results demonstrated that graphene-CNT sample had higher carrier mobility than graphene and a lower resistivity compared to the graphene sample as shown in Figure 16 due to how fast electrons can move through it. The carrier concentration and mobility come from a limited number of electrons that flow with high mobility on graphene-CNT sample.

Figure 16. Mobility vs Resistivity of Graphene and Graphene-CNT.

A total of ten runs were collected as shown in Figure 16, the blue line represent the graphene-CNT and the orange line represent the graphene. Run number 3 of graphene-CNT has a mobility of 347.4 cm2/Vs while graphene has a mobility of 1953 cm2/Vs. This large difference might be due to the open environment where the testing was performed. It is recommended to perform the testing in a vacuum environment and minimize possible contamination. By analyzing the two lines, it could be observed that graphene-CNT has better mobility than pristine graphene sample. Its average mobility is three times higher than the graphene.

Four Point Probes characterization was performed on graphene and graphene-CNT samples to study its sheet resistance. Graphene and graphene-CNT on SiO_2 substrate. The sheet resistance values obtained was as expected for graphene which was estimated to be ~500 Ω/sq. in average [15] and graphene-CNT. The idea of the four point probes is that current passed through the outer probes and induces a voltage in the inner voltage probes as on Appendix 3-2.

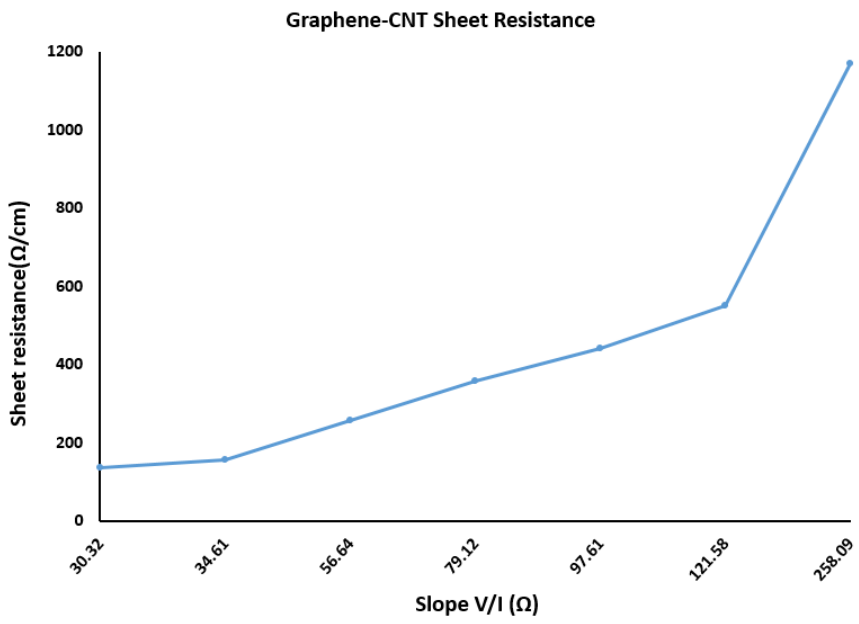

Figure 17. Four Point Probe Plot for Graphene-CNT's Sheet Resistance.

The probes location on the substrate were varied to analyze the surface. The obtained results as shown in Figure 17 and Figure 18. Graphene average sheet resistance of 1460.74 Ω/cm was obtained whereas graphene-CNT average sheet resistance obtained was around 438.86 Ω/cm. Graphene-CNT has lower sheet resistance compared to the average value of graphene.

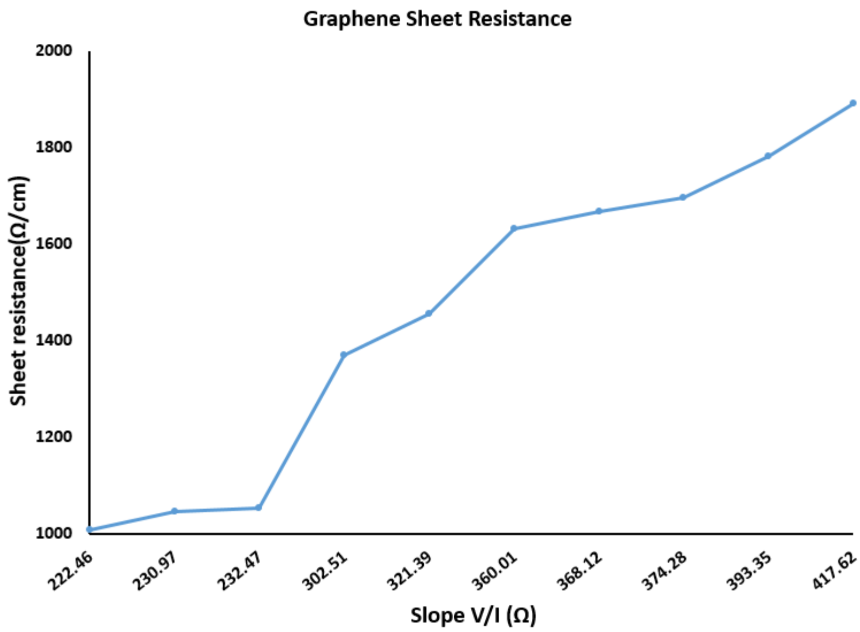

Figure 18. Four Point Probe Plot for Graphene's Sheet Resistance.

The V/I slope versus the sheet resistance was at a range of 1 mA starting current and 5 mA stopping current. It is demonstrated that graphene and CNT hybrid may improve the sheet resistance upon modifying graphene with molecular doping, the sheet resistance of the samples changes from 597 to 221 ohm square, decreasing by 63% of the original value [16].

UV-VIS Spectrophotometer was used to analyze the light transmittance of the samples. PDMS substrate coated with graphene and graphene-CNT film were inserted into the system. The light transmittance of both samples were analyzed from ultraviolet to visible wavelength region. The average light transmittance percentage of bare PDMS alone was 99%. For graphene on PDMS substrate the transmittance was around 97% while for graphene-CNT was 88% approximately as shown in Figure 19.

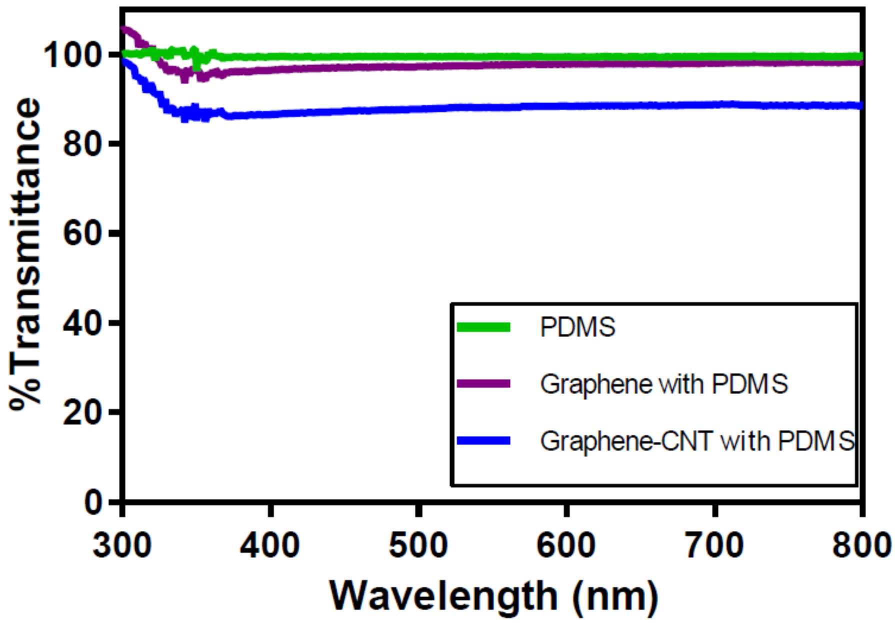

Figure 19. Transmittance percentage of graphene and Graphene-CNT films. Graphene CNT is lower compared to the graphene sample due to the presence of CNT, which cover some areas of the sample.

Other studies confirm the obtained result above that in the visible range of 390 nm to 760 nm, the optical transmittance of the graphene dielectric film was higher than 88%. The optical transmittance at a wavelength of 550 nm was 93%[17]. Few values are above 100% transparency, this discrepancy is due to the base line calibration. The wavelength range of 380 nm to 300 nm is the low visible region. The optical transmission spectra as function of the wavelength shows it has high transmission in the range > 400nm; it demonstrates the highly transparent and conductive characteristics of graphene on PDMS and graphene-CNT on PDMS substrate.

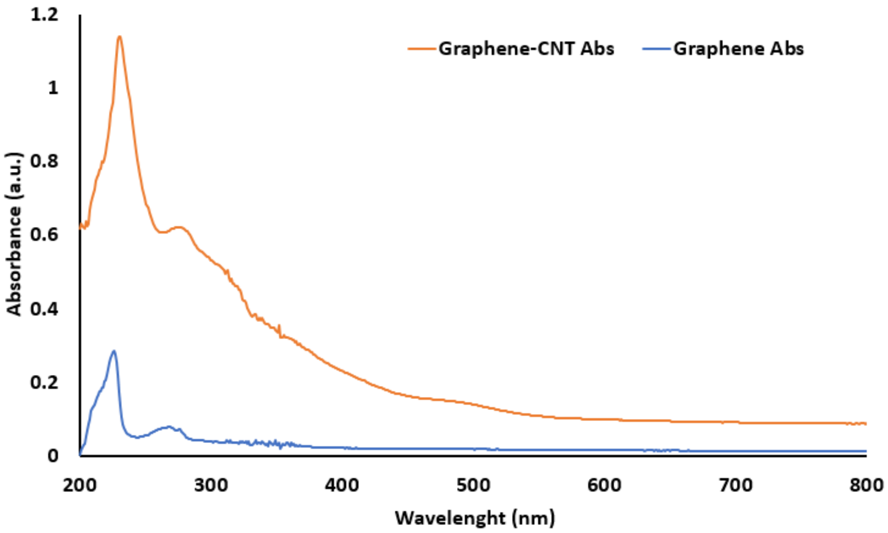

Figure 20. Absorbance wavelength for graphene and graphene-CNT

The absorbance plot shown in Figure 20 proves the lower absorption of lights in the graphene sample compared to graphene-CNTs sample. The absorbance is nearly negligible for 400 nm to 800 nm range, while on the ultraviolet range the absorbance increases a minimum. Graphene-CNTs TCF absorbance is notable on the visible range whereas on the ultra violet range it increases drastically. These result reflect the values of transmittance obtained in Figure 19.

4.2. Discussion

Raman spectra, SEM and TEM were used to confirm the presence and existence of graphene and CNTs on the samples fabricated. Raman peak intensity at D and 2D ratio confirms the existence of single layer graphene shown in Figure 13. The SEM and TEM studied the morphology of the graphene and CNTs as shown in Figure 14 and Figure 15. The electrical characterization results are shown in Table 7 , compared to ITO we concluded that graphene-CNTs can be a possible replacement of ITO.

Table 7. Graphene-CNTs fabricated versus ITO

	Fabricated Samples		**Compared to**
	Graphene-CNTs	**Graphene**	**ITO**
Average Mobility(cm^2/Vs)	3445.74	1633.76	-
Average Resistivity(Ωcm)	$1.28x10^{-5}$	$2.55x10^{-5}$	$1.28x10^{-4}$
Average Sheet Resistance (Ω/cm)	438.86	1460.74	10-350 Ω/sq.
Transmittance (%)	84	97	85

ITO has been grown without oxygen by dc and RF magnetron sputtering techniques on glass substrates and characterize to study its properties. The obtained results of ITO shown in Table 7 gives a transmission in visible region above 85% and the substrate resistivity for the grown films of about $1.28x10^{-4}$ Ωcm and $1.29x10^{-4}$ Ωcm at room temperature [18]

CHAPTER 5

5.1. Conclusion

As conclusion, graphene and graphene-CNT were grown and characterized using the Hall Effect Measurement, UV-Vis and Four Point Probe method. The obtained results demonstrated that graphene-CNT samples have better mobility than the graphene samples.

TEM, SEM and Raman characterization techniques were performed to ensure the existence of graphene and CNT on the thin composites. Figure 14 shows how well combined are graphene and CNT and it shows the lattice structure of graphene. In Figure 15 it shows the length of the CNT wall layers, proving the presence of CNT on the composite film.

PDMS was utilize as a base for graphene and graphene-CNT samples. The samples visibility for graphene on PDMS is about 97% while for graphene-CNT on PDMS is about 88%. This demonstrate the high visibility of the composite on a PDMS substrate.

The unique properties of graphene and graphene-CNT attracts the interest of researcher from various fields. This research will develop flexible graphene-CNT-PDMS TCF that possess good optoelectronic performance, transparency, flexibility and a strong adhesion to substrate. The undertaking of this research will provide the important information on the characteristics of tailor-made graphene and CNT for TCF, transfer method of graphene and CNT onto PDMS and overall performance of the hybrid TCF which will be useful for further research.

CVD graphene meets the most important criteria of abundance, low cost, conductivity,

stability, electrode/organic film compatibility, and flexibility that are necessary to replace ITO[14]. The successful fabrication of this hybrid TCF will provides a path for various applications such as light emitting devices, electrochromic devices, photovoltaics, smart display and touch screen.

5.2. Recommendations

The excellent properties of graphene and CNT composites are attracting researchers making it a promising material in next years as shown in Figure 3 and Figure 4. Carbon nanotubes mechanical properties are still being discovering and debated.

This project focused on the charactirazation of graphene and graphene-CNT composites and its electrical properties, futher studies are required in terms of:

- Mechanical properties in terms of torsion, tensile and strechability.

- Study the effects of placing a layer of graphene on top of CNTs, for this project the CNTs was placed on top of the graphene.

- And fabricate a larger sample to be characterized.

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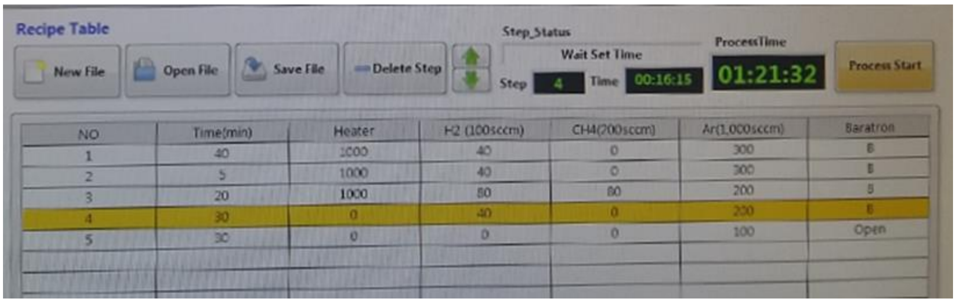
APPENDIX

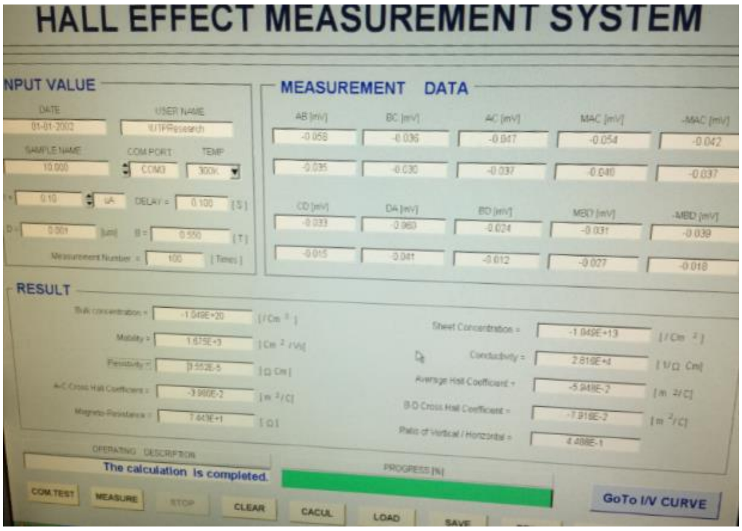
Appendix 1-1: Graphene and graphene-CNT recipe.



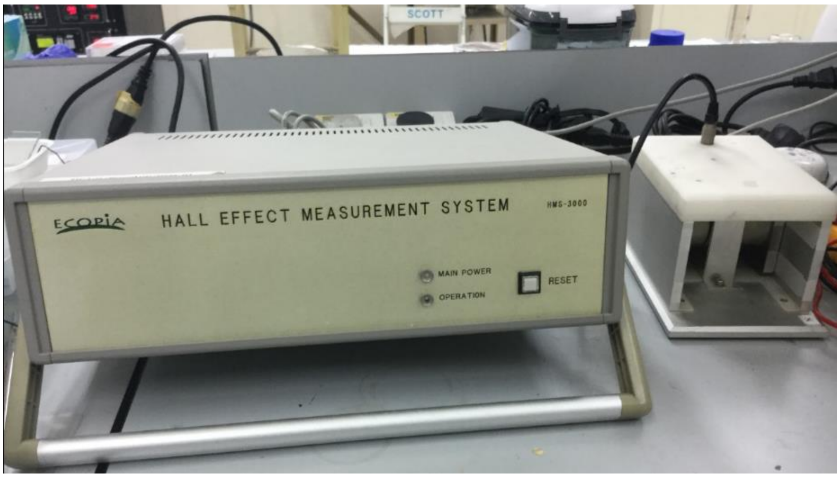
Appendix 1-2: Spin coating machine parameters.

Appendix 1-3: Heating the samples at 80 degrees Celsius.

Appendix 1-4: Hall Effect measurement system parameters.



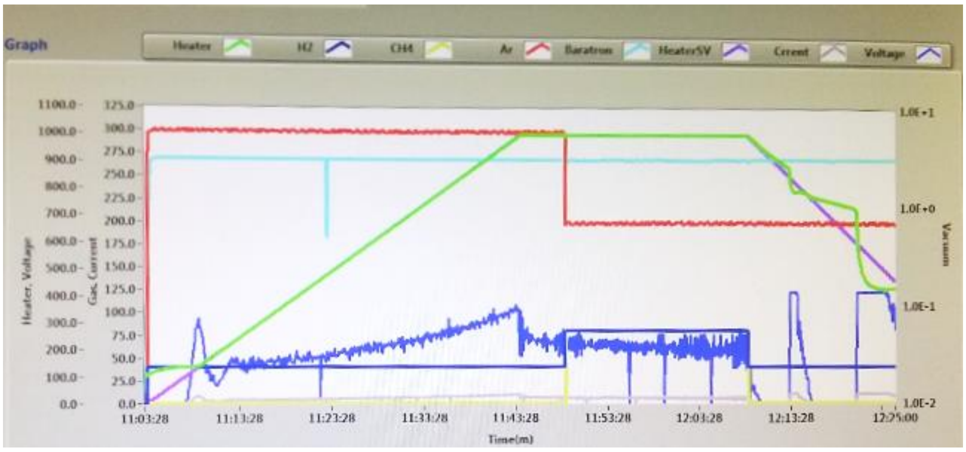
Appendix 1-5: Hall Effect equipment.



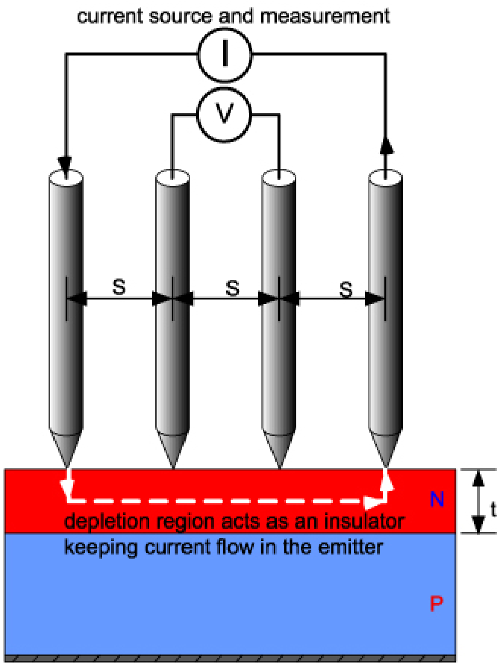
Appendix 2-1: Materials and equipments list.

MATERIALS AND EQUIPMENT	
CONSUMABLES	EQUIPMENTS
Copper foil	SEM and TEM
Iron (III) Chloride	Graphene CVD
PMMA	Spin Coater
Silicone Elastomer	Oven
PDMS	Hall Effect Measurement System
Anisole	UV-Vis Spectrophotometer
	Four Point Probe System
	Raman Spectroscopy
	Digital Multimeter

Appendix 3-1: CVD heater-voltage, gas-current vs time



Appendix 3-2: Four point probe measurement system.



Appendix 4-1: Mold design