DEVELOPMENT OF TRANSPARENT AND FLEXIBLE GRAPHENE COATED ELECTRODE

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To my dearest parents, family, friends, and *you*.

I would not have made it this far without your support, guidance and love.

May this knowledge be useful for others.

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ABSTRACT

Conductive graphene coated film of rubber silicone polymer was prepared using the facile and simple spin coating technique. Graphene coated films have been studied tremendously worldwide and attracted much attention as they have great potential in flexible optoelectronic applications. Traditionally, Indium Tin Oxide (ITO) have been used for decades as electrodes but high mechanical brittleness of ITO makes it unsuitable for flexible devices. Thus, studies on finding the alternatives for ITO increase by time. In this present work, rubber silicone polymer was used as substrate due to its high transparency and flexibility while graphene was used as coating layer as it has great properties. The main aims of this project include to develop high conductivity electrode together with optimum aforementioned properties. Deposition of graphene solution was varied from 1 to 8 drop. Several parameters were used; dispersion duration (1 & 2.5 hours) and coating speed (500 & 1000rpm) obtain the best sample. Longer sonication time produced better dispersed graphene while lower coating speed resulted in better scattered graphene coating. In the present work, Sample 3 with 3 drops of graphene solution was found to have the best properties among all. Conductivity was set to be the most important property, hence was set as the first screening. The highest current value recorded was 0.2 x 10^{2} A at V=10 meanwhile for flexibility test, current value dropped by 100 times as resistivity increased. As drop number increased, the deposition of graphene on substrate increased causing the formation of graphite from graphene. This resulted in very low conductivity for Sample 6, 7, and 8 with current value ~1 x 10^{-9}A which closed to reference sample with current value ~1 x 10^{10}A. However, results obtained are respectively low compared to electrical properties of graphene from literature which will be further discussed in this report. Optical microscope image shows the presence of graphene but agglomeration was spotted on the substrate which explains the low current value in most samples.

ABSTRAK

Polimer silikon getah disaluti graphene telah disediakan menggunakan teknik salutan ringkas. Filem bersalut graphene telah banyak dikaji di seluruh dunia dan menarik perhatian kerana mempunyai potensi besar dalam aplikasi optoelektronik fleksibel. Secara tradisinya, Indium Tin Oxide (ITO) telah digunakan selama beberapa dekad sebagai elektrod tetapi kerapuhan mekanikal yang tinggi menjadikannya tidak sesuai untuk peranti fleksibel. Oleh itu, kajian mencari alternatif untuk ITO bertambah mengikut masa. Dalam kerja ini, polimer silikon getah digunakan sebagai substrat kerana ketelusan dan kelenturannya yang tinggi manakala graphene digunakan sebagai salutan kerana ia mempunyai ciri-ciri yang hebat. Matlamat utama projek ini termasuk untuk menghasilkan elektrod berkonduktiviti tinggi. Jumlah titisan graphene dimanipulasi dari 1 hingga 8 titis. Beberapa parameter digunakan; tempoh penyebaran (1 & 2.5 jam) dan kelajuan salutan (500 & 1000rpm). Masa sonikasi yang lebih lama menghasilkan graphene yang lebih baik sementara kelajuan salutan yang lebih rendah menghasilkan salutan graphene yang lebih baik konsisten. Dalam kerja ini, Sample 3 dengan 3 titisan titisan graphene didapati mempunyai sifat terbaik antara semua. Konduktiviti telah ditetapkan sebagai sifat yang paling penting, oleh itu telah ditetapkan sebagai pemeriksaan utama. Nilai arus tertinggi yang direkodkan ialah 0.2 x 10^2 A pada V = 10 sementara untuk ujian fleksibiliti, nilai arus menurun sebanyak 100 kali apabila resistiviti meningkat. Apabila jumlah titisan meningkat, pemendapan graphene pada substrat meningkat menyebabkan pembentukan graphite dari graphene. Ini mengakibatkan kekonduksian yang sangat rendah seperti Sampel 6, 7, dan 8 dengan nilai arus ~ 1 x 10^{-9} A yang hampi kepada sampel rujukan dengan nilai arus ~ 1 x 10^{-10} A. Walau bagaimanapun, nilai arus yang diperoleh adalah rendah berbanding dengan sifat elektrik graphene dari literasi yang akan dibincangkan dalam laporan ini. Imej mikroskop optik menunjukkan kehadiran graphene tetapi aglomerasi dilihat pada substrat yang menerangkan nilai semasa yang rendah dalam kebanyakan sampel.

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LIST OF ABBREVIATIONS

1D	-	One dimensional
2D	-	Two dimensional
3D	-	Three dimensional
CNT	-	Carbon Nanotube
DCM	-	Dichloromethane
FED	-	Field Emission Display
FET	-	Field-effect Transistors
ITO	-	Indium Tin Oxide
OLED	-	Organic Light-emitting Diode
OM	-	Optical Microscope
PEDOT:PSS	-	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PS	-	Polystyrene
RT	-	Room Temperature
SEM	-	Scanning Electron Microscopy
SWCNT	-	Single Wall Carbon Nanotube
TCE	-	Transparent Conductive Electrode
TEM	-	Transmission Electron Miscroscopy
UV-Vis	-	Ultraviolet Visible

LIST OF SYMBOLS

A	-	Absorbance
Å	-	Angstroms (1Å = $1x10^{-10}$ m)
cm^2	-	Centimeter squared
cm^3	-	Centimeter cubed
°C	-	Degree celcius
eV	-	Electron volt
GPa	-	Gigapascal
I_o	-	Incident radiation
K	-	Kelvin
m/s	-	Meter per second
µm	-	Micrometer
nm	-	Nanometer
Ω*/sq*	-	Ohm per square
TPa	-	Terapascal

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, great attention has been attracted to the synthesis of field emission display (FED) structures materials made from polymers due to their enhanced optical, electrochemical and electrical properties intrinsically associated with their low dimensionality. Materials with a remarkable combination of high electrical conductivity and optical transparency are important components of various optoelectronic devices such as organic light emitting diodes (OLEDs), energy storage and conversion (supercapacitors), batteries, fuel cells, solar cells, and bioscience/biotechnologies [1].

In the case of emission display, these components work as anodes to extract separated charge carriers from the absorbing region, while in the case of OLEDs, they inject charge carriers without affecting the light out-coupling efficiency. Traditionally, Tin-doped Indium Oxide (ITO) and Fluorine-doped Tin Oxide (FTO) have been used for most OLEDs for almost four decades. The ability to deposit these materials with controlled thickness and controlled doping concentration has significantly contributed to their widespread application [1,2].

However, the next generation of optoelectronic devices requires transparent conductive electrodes (TCEs) to be lightweight, flexible, cheap, and compatible with largescale manufacturing methods, in addition to being conductive and transparent. These requirements severely limit the use of ITO as transparent conductors because ITO films fail under bending, restricting their use in flexible optoelectronic devices [2]. In addition, the limited availability of indium sources resulting in ever-increasing prices of indium creates an urgent need to find other materials that can work as transparent conductors for future optoelectronic devices [1].

The question arises: what materials can fulfil these requirements? Having realized the need to replace ITO, the research community has made significant advances in this direction, with identification and evaluation of potential candidate materials. The most significant materials among these are carbon nanotube (CNT) films, graphene films, metal gratings, and random networks of metallic nanowires [3]. Vis a vis, the study on the new contender; graphene, has increased exponentially since it was first isolated in 2004 as it has enhanced the behaviour of polymer especially in electronic applications.

Graphene, a two-dimensional (2D) single layer building block for sp2 carbon allotropes, exhibits remarkable electronic and mechanical properties. The discovery of graphene has revolutionized the field of electronics owing to its excellent and mechanical stability and electronic properties such as high flexibility and optical transmittance, which paves the way for ultrafast electronic devices, bio- and chemical sensors graphene is a single sheet of sp2- bonded carbon atoms. As a zero band gap semiconductor, its electronic structure is unique in the sense that charge carriers are delocalized over large areas, making it a scattering-free platform for carrier transport. High Fermi-velocity and the ability to dope the graphene films externally result in extremely high in-plane conductivities [4].

In this project, various properties of spin-coated graphene film on polymer substrate will be investigated. Conductive films with different layers were made by spin-coating graphene dispersed in dichloromethane (DCM) onto a rubber polymer substrate (1cm x 1cm). Then their properties including morphological, compositional, structural and optical properties of the nanocomposites will be characterized and further discussed.

1.2 Research Motivation

In spite of the tremendous progress of miniaturized electronic technology, further development to soft electronics is still limited by the rigidity of the materials themselves. Electronic devices on flexible and stretchable substrates, defined as soft electronics, are contrasted to traditional rigid chips using conventional substrates and metals. The strategies for developing soft electronics are driven by the investigation of new materials which are bendable, twistable, flexible and stretchable. Toward the basic requirement of replacing traditional rigid silicon electronics by new materials, structure engineering, such as structures in "wavy" layouts and the open mesh geometry have also been investigated to achieve stretchability.

In recent years, graphene has been found as replacement to transparent conductive oxides such as FTO and ITO as flexible electrode displays. Graphene is expected to act as an excellent conducting transparent electrode material because of its extraordinary electrical, thermal, and mechanical properties including a carrier mobility exceeding 10^4 cm^2/Vs and a thermal conductivity of 10^3 W/mK [5,7]. In this work, rubber silicon polymer is introduced as substrate, which meets aforementioned requirements of strong interaction and electrical conductivity. Rubber has perfluoroalkyl backbones which have higher hydrophobicity than the traditional hydrocarbon-based surfactants and may have stronger interaction with graphene than other traditional surfactants.

1.3 Problem Statement

ITO has dominated the transparent electrode market for several decades due to its high transparency and conductivity [1]. It is a commercially dominant transparent conductor with relatively high conductivity (sheet resistance of 10–20 Ω/cm) and transmission (>80%) in the visible region of the solar spectrum. However, brittleness, scarcity of indium and relatively high cost have hindered its application in the emerging fields, such as flexible, stretchable and wearable devices [2].

1.3.1 Increase in Price of Indium

ITO is a ternary composition of indium, tin and oxygen in varying proportions. Depending on the oxygen content, it can either be described as a ceramic or alloy. Indium tin oxide is typically encountered as an oxygen-saturated composition with a formulation of 74% In, 18% O2, and 8% Sn by weight.at However, the scarcity of indium resources in the world and its high demand from the display industry has created large cost fluctuations and future supply concerns [2].

An official report on the market trend of minerals United States Geological Survey (USGS) suggests that the price of indium increased by approximately 25% between 2010 and 2011 from $570/kg reaching a maximum of $780/kg in the U.S. while world-wide production of indium increased only by 5%. The price of indium has fluctuated anywhere between 10 and 40% annually in the past 5 years [2,4]. Apart from the volatility of indium prices, its incorporation in the processing of ITO requires high preparation temperatures and vacuum-based highly energy intensive deposition techniques such as sputtering, thus further increasing the cost of ITO.

1.3.2 Flexibility of ITO

Despite its high conductivity and transparency, ITO is not flexible as it has high mechanical brittleness and will break under little strain that make it unsuitable for flexible electronic devices. Apart from that, it also has bad adhesion to organic and polymeric materials. Gu *et al.* deposited ITO layer on PET substrate and then the substrates were operated bending test (100 times) with various range to study the effect of cyclic bending on ITO films' sheet resistance using four-point probe [6]. They reported that as the radius of bending test decreased, the reduction of device properties, such as current density, brightness, and quantum efficiency. They also found that the sheet resistance of ITO films increased as the radius of bending decreased (Figure 1.1), hence making it not feasible for flexible FEDs [6].

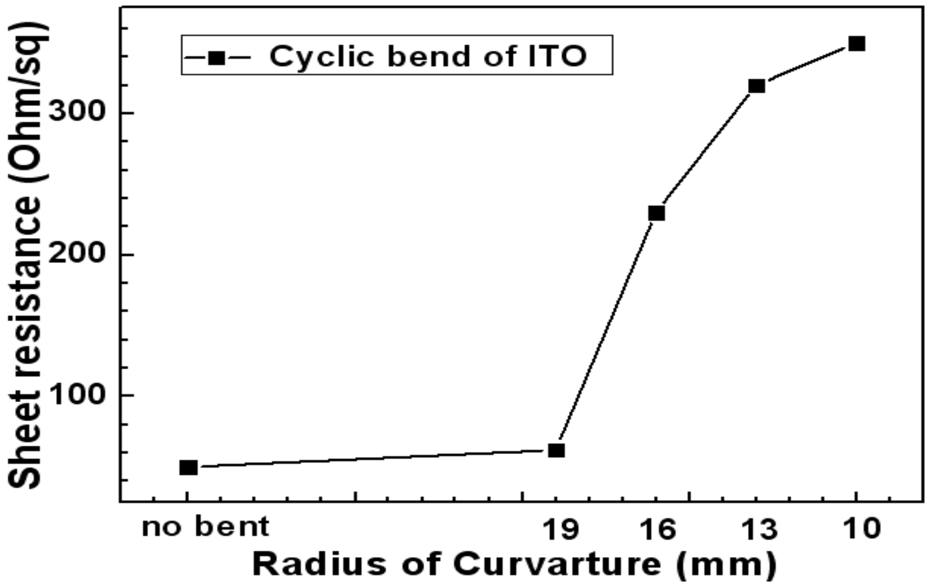

Figure 1.1: Graph of Sheet Resistance against Radius [2]

Thus, alternatives such as conducting polymers, carbon nanotubes, graphene, and metallic networks have been proposed where in this particular report will focus on graphene.

1.4 Research Objectives

The objective is to prepare high transparency and flexibility graphene coated electrode using ion irradiation and spin coating methods.

1. To study the effect on film transparency with respect to the amount of graphene dispersed on each sample.
2. To obtain high conductivity of current improved by the graphene coating.
3. To characterize the morphological, compositional, structural and optical properties of the structure.

1.5 Research Scope

The objective of the project can be obtained through the research scopes that outlined as follows:

1. Fabrication of polymer sheet using polymer & Elastomer (Rubber Silicon Polymer)
2. Coating the surface using spin coating technique
3. Transparency and conductivity analysis
4. Characterization of its mechanical properties

1.6 Research Activities

The implementation of this study has been summarized into a flowchart as shown in **Figure 1.2**. This study is focused on the preparation of the graphene coated substrate made from Silicon Rubber Polymer. Firstly, the preparation of the experimental setup is performed. Graphene then were dispersed in DCM. The film were prepared using spin coating method and its properties will be investigated by varying a few parameters such as amount of graphene dispersed and ultra-sonication time.

Next, the morphological of the film structures will be performed using Optical Microscope. Due to equipment's availability issue and time constraint, characterization using SEM and TEM was not possible. Meanwhile, the electrical properties were characterized using 2 probe tester and the transparency were studied qualitatively. All data collected was analysed.

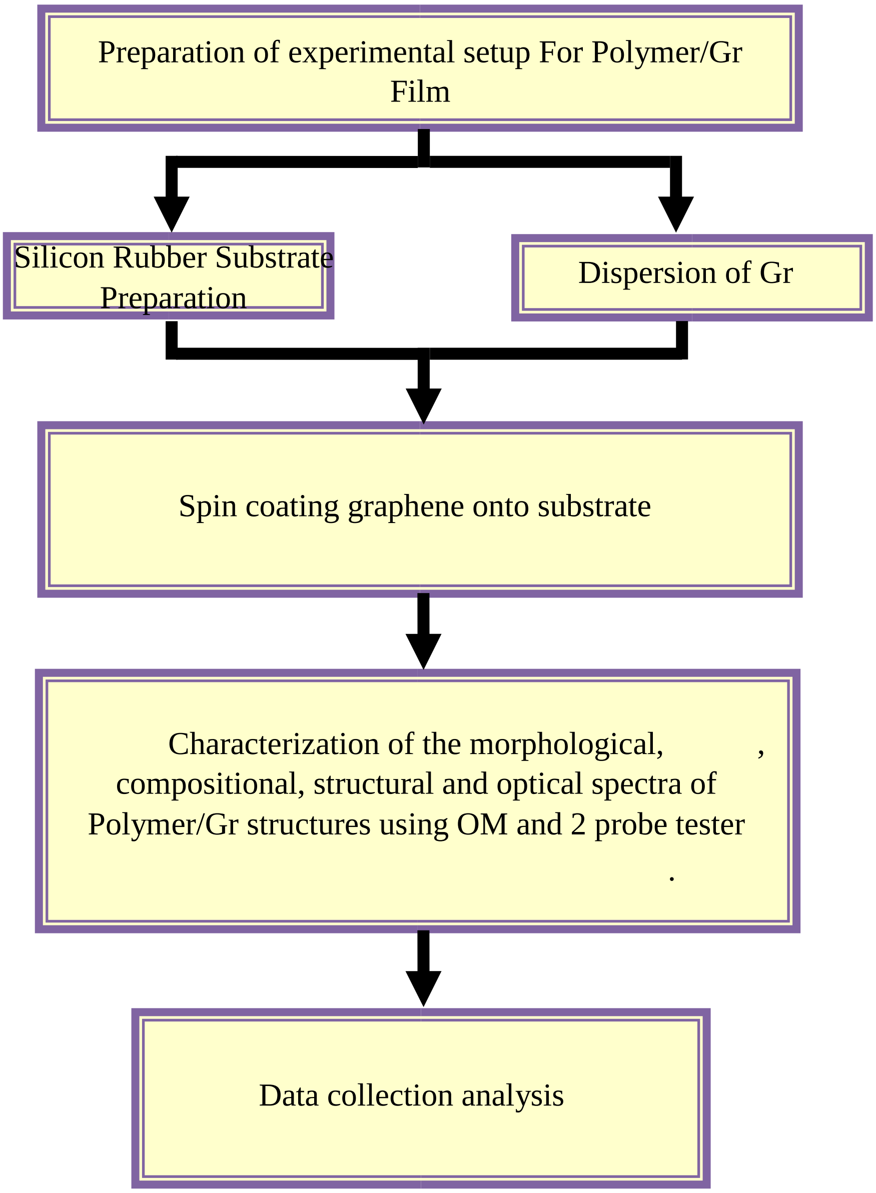

Figure 1.2: Research Activities

1.7 Significance of Research

This research addresses various electronic sectors' strategic objectives. It includes achieving maximum plant useful life and cost/risk-focused decision making in regulation, operation, and design. This research also focuses on developing a methodology to address materials degradation/aging.

The preparation technique can be a cost effective, less tedious method for real life applications. Conventional method such as using ITO is assumed to obsolete soon due to cases mentioned before. Thus, finding such alternatives is vital.

1.8 Thesis Overview

This thesis is organized into 5 chapters. Chapter 1 gives a brief introduction of the research background on the application of flexible devices, problem statements. The objectives, research scopes and research activities are also presented.

Chapter 2 presents a comprehensive review of literature on the ITO and graphene properties together with their application. The first part of this chapter explains the structural, optical and electronic properties of ITO in order to provide in-depth knowledge of ITO materials. Then it briefly explains the need to replace ITO and candidate materials in research world today. Method and application of graphene then are discussed together with nanostructures.

In chapter 3, the details of experimental procedures in this research are described. The substrate preparation and the experimental setup are explained in the first part. Second parts describe the coating procedure with its parameter. The characterization techniques and equipment used are mentioned in the last part.

In chapter 4, results obtained from characterisations are analysed and discussed in details. The effect of drop numbers on samples conductivity and transparency are described which following the objectives of this project. Other than that, the effect of flexibility on samples conductivity are also discussed. The last part shows the analysis of samples' morphology.

Finally, chapter 5 concludes the results obtained and discusses the future research directions.

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