

**FABRICATION OF HYBRID ZNO/TIPS-PENTACENE  
ORGANIC BASED DIODE USING SPRAY COATING  
TECHNIQUE**

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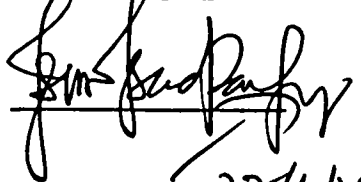
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## ABSTRACT

Organic material is one of the main attraction in recent electronic device applications for smartphone, tablet, and computer due to its high mobility, air stability, and solution processability. This will allow researchers to focus on organic semiconductor in order to achieve the aim for large area application, light weight, and mechanically flexible. This thesis describes analysis and characterization of hybrid ZnO/TIPS-Pentacene organic based diode using several deposition techniques such as drop, dip and spray coating technique. TIPS-Pentacene powder was diluted with Dichloromethane, Chloroform, and Toluene to form weight percentage of 0.1wt%, and 0.2wt%. Disposable spray bottle and airbrush spray were used to analyze the spraying pattern droplet effect to achieve crystalline TIPS-Pentacene thin film. Airbrush spraying technique was chosen as the deposition technique as it can be applied for large coverage and edge area, roll-to-roll process and even thickness. Analysis dependence of deposition parameter was performed to find optimum thin film quality such as distance from nozzle to substrate, number of spray passes and inlet gas pressure used. Optimum distance from nozzle tip to substrate distance was 10 cm with 10 spray passes and 10psi of gas pressure. The thin films were investigated by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and surface profilometer to reveal the film molecular and structure orientation. The spray coated thin films exhibited (0 0  $\lambda$ ) diffraction peaks at  $5.34^\circ$  with d-separation of  $16.4 \text{ \AA}$  that comparable to thermal evaporation method. The surface roughness of deposited thin films varies from 48.7nm to 158nm and grain boundaries between 7nm to 8nm. Following with that, an organic device was fabricated in order to investigate the electrical characteristics. The device structure of ITO/TIPS-Pentacene/Al with 0.1 and 0.2 wt% was constructed and exhibited non-linear behaviour at a low voltage while linear behaviour at a high voltage which similar to conventional p-n junction diode. Furthermore, analysis of electrical characteristics was done to investigate the device performance. The ideality factor ( $n$ ) and barrier height ( $\Phi_b$ ) at different wt% found to be 14.62 and 13.25, 1.1eV and 1.48 eV respectively. Hybrid diode was fabricated with different device architecture of ITO/TIPS-Pentacene/ZnO/Au, ITO/TIPS-pentacene/ZnO and ITO/ZnO/TIPS-Pentacene. ITO/TIPS-Pentacene/ZnO/Au was found to show excellent electrical characteristic among others with low turn on voltage of 0.55V, small value of ideality factor (11.53) and barrier height (1.19eV). Spray coating technique can be the alternative technique for solution process and applied for roll-to-roll device fabrication with desired quality of thin film and good electrical performance.

## ABSTRAK

### **PENGHASILAN DIOD HIBRID ZNO/TIPS-PENTASENA BERASASKAN ORGANIK MENGGUNAKAN TEKNIK SEMBURAN**

*Bahan organik merupakan tumpuan utama dalam aplikasi peranti elektronik sejak kebelakangan ini di dalam teknologi telefon pintar, tablet dan komputer berdasarkan nilai mobiliti yang tinggi, kestabilan terhadap udara dan kebolehan pemrosesan menggunakan cecair. Hal ini membolehkan penyelidik untuk memberi fokus di dalam bidang semikonduktor organik untuk mencapai matlamat aplikasi ruang yang luas, ringan, dan mekanikal fleksibel. Tesis ini menerangkan tentang analisis dan pencirian diod hibrid ZnO/TIPS-Pentaseena berasaskan organik menggunakan beberapa teknik pemendapan seperti titisan, rendaman dan semburan. Serbuk TIPS-Pentaseena telah dicairkan dengan Diklorometana, Kloroform dan Toluena untuk membentuk peratusan berat 0.1wt% dan 0.2wt%. Botol semburan pakai buang dan semburan berus udara telah digunakan untuk menganalisis kesan corak titisan semburan bagi menghasilkan filem nipis kristal TIPS-Pentaseena. Teknik semburan berus udara dipilih sebagai teknik pemendapan kerana ia boleh mencapai ruang yang sempit dan luas, proses berterusan dan ketebalan yang sekata. Analisa kebergantungan bagi parameter pemendapan telah dilaksanakan untuk mencari kualiti filim nipis yang optimum seperti jarak muncung senapang dengan substrat, bilangan semburan dan nilai tekanan gas masuk. Jarak optimum antara muncung senapang dengan substrat adalah 10cm dengan 10 bilangan semburan dilepaskan menggunakan 10psi tekanan udara masuk. Penyelidikan terhadap filem-filem nipis dilaksanakan menggunakan Pembelauan Sinar-X(XRD), Mikroskop Imbasan Elektron(SEM), Mikroskop Daya Atomik(AFM) dan permukaan profiler untuk memperlihatkan orientasi molekul dan struktur filem. Filem nipis terhasil menunjukkan corak puncak pembelauan (0 0 1) pada  $5.34^\circ$  dengan penjarak-d  $16.4 \text{ \AA}$  setanding dengan kaedah titisan. Kekasaran permukaan filem nipis yang terbentuk berbeza-beza dari 48.7nm hingga 158nm dan sempadan butiran antara 7nm hingga 8nm. Sehubungan dengan itu, peranti organik telah dibina untuk menyiasat ciri-ciri keelektrikan. Struktur peranti yang dibina menggunakan ITO/TIPS-Pentaseena/Al menggunakan peratusan berat 0.1 dan 0.2wt% mempamerkan aktiviti tidak linear pada voltan rendah manakala aktiviti linear pada voltan tinggi yang menunjukkan persamaan dengan diod konvensional simpang p-n. Tambahan pula, analisis ciri-ciri keelektrikan telah dilakukan untuk menyiasat prestasi peranti. Nilai faktor idealiti ( $n$ ) dan ketinggian halangan ( $\Phi_b$ ) pada peratusan berat yang berbeza didapati adalah 14.62 dan 13.25, 1.1eV dan 1.48eV. Diod hibrid telah direka-bentuk menggunakan seni bina berlainan seperti ITO/TIPS-Pentaseena/ZnO/Au, ITO/TIPS-pentaseena/ZnO dan ITO/ZnO/TIPS-Pentaseena. ITO/TIPS-Pentaseena/ZnO/Au menunjukkan ciri-ciri keelektrikan yang baik berbanding peranti lain dengan voltan pemula yang rendah pada 0.55V, nilai faktor ideality (11.53) dan ketinggian halangan (1.19eV). Kaedah semburan merupakan teknik alternatif bagi proses cecair dan diaplikasi untuk penghasilan kualiti filim yang dikehendaki dan prestasi keelektrikan yang baik.*



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## LIST OF ABBREVIATIONS

OLED	organic light emitting diode
OPV	organic photovoltaic cells
OLAE	organic large area electronics
ESD	electrostatic spray deposition
SPD	spray pyrolysis deposition
OFET	organic field effect transistor
TFT	thin film transistor
MOM	metal-organic-metal
OTFT	organic thin film transistor
CVD	chemical vapour deposition
HOMO	highest occupied molecular orbital
LUMO	lowest un-occupied molecular orbital
CVD	chemical vapour deposition
ALE	atomic layer epitaxy
FWHM	full width half maximum
PET	polyethylene terephthalate
ITO	indium tin oxide
ZnO	zinc oxide



## LIST OF SYMBOLS

$E_v$	Energy valence band
$E_c$	Energy conduction band
$E_g$	Energy band gap
eV	electron volt
$^{\circ}\text{C}$	Celsius
K	Kelvin
Cm	Centimetre
V	Volt
s	Second
k	Boltzmann's constant
$\rho$	density
$\Omega$	Ohm
%	percentage
A	Ampere
n	integer (1, 2, 3,...)
$\lambda$	wavelength
$\theta$	Bragg diffraction angle
$\beta$	Width of FWHM
$I_0$	saturation current
$R_s$	series resistance
$^{\circ}$	degree
$\text{\AA}$	Angstrom
$\phi_b$	barrier height
$\sigma$	sigma
$h$	distance
J	Joule
a.u	arbitrary unit
$A^*$	Richardson constant
h $\nu$	photon energy
m	metre
h	Planck constant
q	electron charge





T	Absolute temperature
I	Current
$\alpha$	absorption coefficient
B	Full Width Half Maximum
A	Area



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# CHAPTER 1

## INTRODUCTION

### 1.1 Background Study

Organic semiconductor is an organic material, which exhibits semiconductor properties. It is divided into two groups of "linear backbone" polymers and small molecule. The combination of organic materials and solvent use to fabricate semiconductor device leads to good electrical performance and mechanical benefits. Researchers are focussing on organic semiconductor to achieve the aim for large area, light weight, mechanically flexible and potentially low-cost electronics with several numbers of application such as televisions, smartphones, portable media players and radio frequency identification tags (Zheng *et al.*, 2015, Wolak; Jang, 2004; Nam *et al.*, 2010)

The interest in the study of organic device fabrication is due to these devices are easier to fabricate than conventional silicon-based device that require various processed techniques and expensive (Cherenack, 2009). Research invention on organic semiconductor was done and leads to the simple fabrication process which is solution processed method and the organic material is known as soluble organic semiconductor.

Among soluble organic semiconductors, the solution processed small molecules such as TIPS-Pentacene exhibits high carrier mobility in organic thin film



transistor and efficient p-type organic semiconductor (Sakamoto, *et al.*,2012; Doi, *et al.*, 2012; James *et al.*, 2011). The device performance is determined by how well the TIPS-Pentacene molecules are ordered for  $\pi$ -electrons to sufficiently overlap each other during drying. The hole mobility in TIPS-Pentacene is largely dependent on crystal orientation and crystal quality, such as the size of single crystal domains and the crystal thickness. These physical parameters are influenced by the choice of solvent, solution concentration and deposition method.

There are various cost-effective solution deposition techniques to fabricate thin film such as drop casting, inkjet printing and spray coating. However, each fabrication techniques differ from another by the droplet size, liquid drop impact and speed impact of the droplet hence resulting in different molecular orientation and device performance.

## **1.2 Problem Statement**

Organic electronics received high attention for its application, performance and the aim for mass production. However, there are several problems which have largely restricted the further application of organic materials such as slow fabrication process, difficult edge coverage and uneven surface morphology.

Pentacene organic semiconductor is known by its excellent mobility, researchers take a step ahead to make it soluble by adding functional TIPS group to the main chain. Therefore, solution-process organic semiconductor can be promoted as cost effective fabrication technique for large area of fabrication for low-cost electronic devices. However, small molecule materials are dependently on solvent properties to form a molecular oriented thin film. High boiling point solvents are preferred for slow drying solution process to form fewer nuclei and larger crystal possible.

Drop cast technique is the earliest technique used in organic deposition using solution process to produce crystalline thin film with a good molecular ordering, but the thin film exhibits random crystal formation, big gaps and aggregation. On the other hand, inkjet-printed technique is introduced to enhance the drop casting technique since the ejection of a jet ink can produce overlap droplet and design the desired crystal forming direction hence increase the mobility for device's application. However, in large area production, it is not preferable because the technique takes a longer time to form a thin film due to each droplet to crystallize. Therefore, spray coating technique is preferable for roll-to-roll process and large area application. Spray coating technique is implemented with several controlled parameters such as spray nozzle size and shape, atomizing gas pressure and solution properties in order to achieve better organic deposited thin film crystallinity. A better deposited thin film will enhance the electrical performance of organic devices. Thus, investigation of thin film deposited by spray coating diode device will be carried out.

Semiconductor devices fabricated using inorganic and organic conduction layer will produce slightly different electrical performance due to adhesion between each layer, layer height, overlapping between molecular structure and organic crystallinity. Thus, electrical characteristics based on diode structure of spray coated organic thin film were carried out to investigate the relationship between organic layer crystallinity and device performance.

### **1.3 Research Objective**

This research aims to develop a two-terminal organic p-n diode using organic semiconductor by spray coating fabrication technique. This research work is accomplished through following objectives:

- i. To characterize the structural and morphology of organic thin film fabricated by spray coating technique.
- ii. To evaluate the effect of solvent and solution concentration on the structural properties of organic thin film.

- iii. To evaluate the electrical performance of fabricated diode on flexible substrate.

Organic diode requires different type of semiconductor layers, which organic semiconductor as p-type and inorganic semiconductor as n-type semiconductor will be fabricated. Extraction from a p-n (TIPS-Pentacene and Zinc Oxide) diode electrical characteristics reveals the device performance in order to achieve the closest ideal diode parameter.

#### **1.4 Research Scope**

This research is conducted using two types of spray coating apparatus such as disposable spray bottle and airbrush spray system. Powder-based organic semiconductor material is diluted in organic solvent with different solution concentration to perform the measurement and characterization of thin film. The smallest sample size achieved is 3×3cm determined by the dispersion area of spraying solution. The fabrication and current-voltage measurements of a device was done in ambient air condition without clean room but provision steps taken to minimize contamination.

#### **1.5 Thesis Outline**

This thesis is consisted of five chapters. Chapter 1 is an introduction of organic semiconductor and recent technologies applied in commercial products and several techniques conducted via solution process in the research area. The research aim, objective and scope of this thesis are also presented in this chapter.

Chapter 2 describes about fundamental theory of semiconductor physics. Several solution process commonly used in thin film fabrication and technique used in this experiment is briefly described. Instruments used for analysis and characterization such as X-Ray Diffraction (XRD), Surface Profiler LS500, UV-Vis and I-V Keithley are also explained to reveal the physical and electrical characteristics of fabricated diode.

In chapter 3, explanation on experimental setup including chemical preparation, substrate cleaning and parameter used for each thin films deposited by spray coating and sputtering machine is provided.

In chapter 4, output result obtained for each characterization for physical and electrical briefly analyzed. Relation between electrical characteristics and physical properties of fabricated devices have been discussed. Relation between electrical performance and different device configuration was investigated.

Chapter 5 is the conclusion for this experiment. All results obtained from the experiments were summarized and relation between physical and electrical properties were discussed. A few recommended steps were discussed for enhancement in future work.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Overview

Organic semiconductor can be divided into small molecule (low weight), oligomer and polymer. The chemical properties of organic semiconductor will determine their solubility in organic solvents and the deposition techniques will affect the organic semiconductor thin film crystallinity. In this chapter, a general description of crystalline materials and the arrangement of organic crystal, followed by an introduction to the working principles of semiconductor materials will be discussed. Then, the concepts of organic semiconductor, the type of organic semiconductors, energy band diagram and Fermi energy level will be discussed. Later, various deposition techniques for soluble organic semiconductor are reviewed. Furthermore, the organic semiconductor devices with respect to their electrifying performances are also reviewed.

#### 2.2 Organic Semiconductor

Organic semiconductors are formed using organic materials, which show semiconductor properties, rather than exhibit as insulators as many organic compounds do. It is because of the valence electrons in most organic compounds are very tightly bound and fixed in place in covalent bonds between individual atoms. However, these organic compounds may exhibit as semiconductors when the electrons exhibit a high degree of delocalization while a high degree of conjugation occurred in the molecular core of large aromatic compounds. There is a formation that consist a pair of  $\pi$  molecular orbitals when the  $\pi_{pz}$  orbitals in carbon-carbon double bonds of unsaturated organic compounds overlap. The lower energy





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