FABRICATION OF THIN FILM AND METAL-ORGANIC-METAL (MOM) DIODE USING PTAA-TIPS-PENTACENE

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PERPUSTAKAAN UNIVERSITI MALAYSIA SABAH SABAH

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HOH HANG TAK

THESIS SUBMITTED IN FULFILLMENT FOR THE DEGREE OF MASTER OF ENGINEERING

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DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, equation, summaries and references, which have been duly acknowledged.

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ABSTRACT

The organic semiconductors potentially offer attractive characteristics, such as lowtemperature fabrication, flexibility deposition technique, low-cost processing, and lightweight, which can be used as an active component in a wide range of electronic applications. Recently, organic semiconductors have gained the attention to facilitate formation of thin film by using solution-processed deposition techniques. The solutionprocessable organic material such as poly(triarylamine) (PTAA) and 6,13bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) have been reported to exhibit low mobilities, which far comparable to that of vacuum-deposited organic semiconductors mainly due to the morphology of thin films. To achieve device performance to a higher level, morphology design and control by varying spin-coating condition such as spin speed is crucial. The MOM diode was designed by forming a PTAA-TIPS-pentacene layer based on the concentration of TIPS-pentacene, i.e. 0 %, 5 %, 10 %, 15 %, and 20 % in PTAA, between the indium tin oxide (ITO) electrode layer and the counter aluminium (AI) metal layer. X-ray diffraction (XRD) patterns revealed that with the intensity of diffraction peak for PTAA was increased by increasing the pentacene molecules in PTAA. This indicated that there is a binder effect between PTAA and TIPS-pentacene enhance the molecule ordering. Furthermore, the current-voltage (I-V) characteristics were measured using Keithley 2400 source meter unit from -10 to +10 V. Meanwhile, the frequency dependent electrical characteristics were measured using a precision LCR meter in the frequency up to 100 kHz. The turnon voltage varies from 2.16 to 2.48 V depending on the concentration of TIPSpentacene in PTAA semiconductors, respectively. The frequency dependence of the electrical responses is attributed to the distribution density of interface states that could follow the alternating current (AC) signal. Investigation exposed that conductance was strongly dependent on the frequency and bias voltage. The capacitance and series resistance were dependent up to constant value at the low frequency region (< 1 kHz), but the capacitance and series resistance were independent at high frequencies (< 100 kHz). The MOM diode showed the positive clamping circuit, where the diode discharges when input voltage in the negative side and charging when input voltage is positive side. In conclusion, blending small molecule organic semiconductors into semiconducting polymer have shown the improvement in electrical properties due to the influence of polymer binding on thin film uniformity and operational stability.

ABSTRAK

Semikonduktor organik menawarkan ciri-ciri yang menarik dan berpotensi, seperti fabrikasi pada suhu rendah, fleksibiliti dalam teknik pemendapan, pemprosesan pada kos rendah, serta ringan, yang boleh digunakan sebagai komponen aktif dalam pelbagai aplikasi elektronik. Pada masa kini semikonduktor organik telah mendapat banyak perhatian untuk memudahkan penghasilan filem nipis dengan menggunakan teknik pemendapan daripada larutan. Semikonduktor organik secara pemprosesan larutan seperti poly(triarylamine) (PTAA) dan 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) mempunyai nilai mobiliti rendah berbanding dengan semikonduktor organik menggunakan teknik pemendapan vakum disebabkan oleh morfologi filem nipis. Untuk mencapai prestasi peranti ke tahap yang lebih tinggi, rekabentuk dan kawalan morphology berdasarkan teknik pemendapan seperti kelajuan putaran amatlah penting. Diode MOM direka dengan membentuk lapisan PTAA-TIPSpentacene berdasarkan kepekatan TIPS-pentacene iaitu 0%, 5%, 10%, 15% dan 20% dalam PTAA, di antara oksid tin indium (ITO) elektrod dan logam aluminium (Al) elektrod. Corak difraksi sinar-X (XRD) mendedahkan bahawa intensiti puncak difraksi untuk PTAA telah bertambah dengan peningkatan molekul pentacene dalam PTAA. Ini menunjukkan bahawa terdapat kesan pengikat antara PTAA dan TIPS-pentacene telah meningkatkan susanan molekul. Selain itu, ciri-ciri arus-voltan (I-V) telah diukur menggunakan Keithley 2400 unit sumber meter dari -10 V hingga +10 V. Frekuensi bersandar kepada ciri elektrik tergantung telah diukur dengan menggunakan meter LCR berfrekuensi sehingga 100 kHz. Voltan hidupan berbeza-beza dari 2.16 ke 2.48 V bergantung kepada campuran TIPS-pentacene dalam PTAA. apabila kepekatan TIPSpentacene meningkat 0 %, 5 %, 10 %, 15 %, dan 20% ke dalam PTAA semikonduktor. Frekuensi bersandar kepada sambutan elektrik adalah disebabkan oleh ketumpatan agihan keadaan antara muka yang boleh mengikut isyarat arus ulang alik. Penyelidikan mendedahkan bahawa kealiran adalah amat bergantung kepada frekuensi dan voltan pincang. Kemuatan dan rintangan siri adalah bergantung ke satu nilai tetap di frekuensi rendah (< 1 kHz) tetapi kemuatan dan rintangan siri adalah tidak bersandar pada frekuensi tinggi (< 100 kHz). Diod MOM menunjukkan litar penjepit positif, di mana diod menyahcas apabila voltan input di sisi negatif dan mengecas apabila voltan masukan di sisi positif. Sebagai kesimpulan, pengadunan molekul kecil semikonduktor organik ke dalam polimer semikonduktor telah menunjukkan peningkatan dalam sifatsifat elektrik disebabkan oleh pengaruh polimer pengikatan supaya keseragaman filem nipis dan kestabilan operasi terhasil.

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LIST OF ABBREVIATIONS

RFID	Radio Frequency Identification		
IoT	Internet-of-Thing		
AC	Alternating Current		
DC	Direct Current		
BJT	Bipolar Junction Transistor		
FET	Field-Effect Transistor		
I _{BE}	base-emitter current		
I _{CE}	collector-emitter current		
V_{GS}	gate-source voltage		
I _{DS}	drain-source current		
V _{in}	input voltage		
V _{out}	output voltage		
Ev	valence band		
Ec	conduction band		
Eg	Energy band gap		
MOM	Metal-Organic-Metal		
MIS	Metal-Insulator-Semiconductor		
MPS	Metal-Polymer-Semiconductor MALAYSIA SABAH		
HOMO	Highest Occupied Molecular Orbital		
LUMO	Lowest Un-occupied Molecular Orbital		
SCLC	Space Charge Limited Current		
ILC	Injection Limited Current		
FWHM	Full Width Half Maximum		
sccm	Standard Cubic Centimetre Per Minute		
eV	electron volt		
°C	Celsius		
К	Kelvin		
cm	Centimetre		
V	Volt		
S	Second		
Ω	Ohm		
Hz	Hertz		

LIST OF SYMBOLS

π	pi
h _f	final thickness
k	mass transfer coefficient
C ₀	initial solids concentration
W	spin speed
β ₀	initial kinematic viscosity
ρ	density
h _o	blade height
ΔP	slurry pressure head
μ	fluid viscosity
U	blade speed
L	channel length
j	current density
%	percentage
rpm	Revolutions per minute
A	Ampere
W	Watt
N	integer (1, 2, 3,)
λ	wavelength
θ	angle
d	Spacing between plane
D	average grain size
β	Width of FWHM
I _O	prefactor current
n	ideality factor
Øb	barrier height
Eg	band gap energy
X_{s}	electron affinity of the semiconductor
Y	admittance
Ζ	impedance
G	conductance
ω	angular frequency

f	frequency
С	capacitance
R _s	series resistance
0	degree
Å	Angstrom
σ	electrical conductivity



CHAPTER 1

INTRODUCTION

1.1 Background Study

Organic semiconductor has received a fast growing interest with the advantages of large area, light weight, low-temperature fabrication, flexibility deposition technique, and potentially low-cost electronics that make the field simultaneously challenging and exciting towards the realization of environmentally sustainable electronic devices. Organic semiconductors have been proposed for several numbers of applications such as flexible display for televisions or smartphones, portable media players, rollable solar cell, wireless devices, and radio frequency identification (RFID) tags (Ye et al, 2015). For example, organic solar cells or photovoltaic devices fabricated on flexible substrates such as plastics or metal foils will create new applications on curved surfaces on building, human body, vehicles and portable electronics. Moreover, the organic semiconductor layer possess advantages such as light weight and easy to attach to any part or surface and thus very useful for wireless devices and sensors for internet-of-thing (IoT) applications.

Electronic components can be divided into two-terminal and three-terminal. A diode is one of the two-terminal electronic devices, which has low resistance to allow the current flow in forward direction, and high resistance in the reverse direction in order block the current flow back. So, the diode has the same function of check valve in electronic version. This type of behavior is called rectification. It used to convert an alternating current (AC) to direct current (DC). By using two or more diodes to form full-wave rectification circuit which converts full AC wave into DC. Meanwhile, a transistor is a three-terminal electronic component. It categorized into Bipolar Junction Transistor (BJT) and unipolar transistor such as Field-Effect Transistor (FET). BJT terminals are labeled as base, collector, and emitter. A small base-emitter current (I_{BE}) can control and switch the collector-emitter current (I_{CE}). FET terminals are gate, source, and drain. The gate-source voltage (V_{GS}) can control the drain-source current (I_{DS}). There are two common functions for the transistor. Transistor as an electronic switch in the circuit is one of the function. By increasing the base voltage, the I_{CE} also increases. The collector voltage decrease and nearly no voltage difference to emitter voltage, the current can flow from collector to emitter freely. When saturated, the transistor is switched on. Another function of transistor is as an amplifier. The common-emitter amplifier is designed base serve as input, collector serve as output, and the emitter serve as grounded with both. The change in input voltage (V_{in}) will decide transistor is switched on or off, which decide the flow of supply voltage and create a large change in output voltage (V_{out}).

Organic semiconductor is the materials, mainly made up by chains of carbon, hydrogen, nitrogen, sulfur, and oxygen atoms, and shows properties typically associated with semiconductor properties. Most organic materials are less expensive to create than high crystalline inorganic materials. It also might fabricate devices with low-cost fabrication methods. Organic semiconductor is further divided into two categories, which are semiconducting polymers and small molecules which will further explain in Chapter two (Zaki, 2015). The small molecule organic semiconductor materials are like 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPSpentacene), Tetracene, and Anthra[2,3-b:6,7-b']dithiophene (ADT). On the other hand, the polymer organic semiconductor materials are like Poly(triarylamine) (PTAA), Poly[[5-(2-ethylhexyl)-5,6-dihydro-4,6-dioxo-4H-thieno[3,4-c]pyrrole-1,3diyl](4,4'-didodecyl[2,2'-bithiophene]-5,5'-diyl)] (PBTTPD), and Poly(3hexylthiophene-2,5-diyl) (P3HT).

In particular, most organic materials are soluble in solvents that allows for the opportunity for solution processing which can produce many devices at a fraction of the cost. In addition, most devices require an annealing step to reach high performance that is generally at high temperatures at least 500 °C for silicon,

but is much less or not required for organic materials (Zhang et al, 2013.). One of the advantages for deposit organic materials in solution form is the wide range of thin-film coating technologies already applied by existing industries (Sahu et al, 2009). These include inkjet technique and also a screen printing technique for an individual substrate and extend to continuous roll-to-roll manufacture. The existence of mature, low-cost, and large-area manufacturing routes means that scaling-up of organic semiconductor technology is usually expected to be a quite cheap process.

1.2 Problem Statement

Now a day, solution-processed deposition techniques used to fabricate organic semiconductor materials thin film have getting more and more interest. However, there are several problems which need to be solved in order to improve the organic semiconductor materials performance in the application. The solution-processable organic semiconducting materials such as poly(triarylamine) (PTAA) and 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) have been reported to show low mobility (Intaniwet et al, 2011). The morphology of the organic semiconductor layer has an influence on the device performance. To achieve device performance to a higher level, morphology control by varying deposition condition such as spin speed to vary thickness is crucial.

In solid-state physics, the carrier mobility characterizes how fast the carrier moves through the metal or semiconductor when it pulled by an electrical field. By increasing voltage which in DC, the electric field also increases. By analysis the DC electrical response, the mobility of the carriers in the organic materials was investigated. On the other hand, AC describes the flow of charge that changes polarity or direction periodically. By changing the frequency, the investigation of AC conductivity is needed to investigate the real and imaginary parts of the electrical modulus on spin-coated organic semiconductor layers and how the organic materials to orient with the oscillations of an external alternating electric field.

1.3 Research Objective

This research aim is to investigate the structural property and electrical response of soluble blended organic semiconductor thin films using spin-coating deposition techniques for MOM diode application. This research work can be completed through the following objectives:

- To design blended organic semiconductor thin film-based diode.
- To fabricate blended organic semiconductor thin film-based diode using metal-organic-metal structure.
- To evaluate the structural property and electrical response of blended soluble organic semiconductor thin film-based diode device on glass substrate.

1.4 Research Scope

This research focus on design, fabrication and characterization, which conducted to determine the optimum percentage of TIPS-pentacene blended in the PTAA during deposition that will optimize the DC electrical characteristics and AC frequency-dependent impedance characteristics of the metal-organic-metal (MOM) diode. In the process of diode fabrication, spin coating technique was used as the organic semiconductor material deposition technique to form thin film or layer. The ability of spin coater can quickly and easily form uniform thin films. Thus, spin coating technique requires organic materials which easily to be dissolved in solvent. As a result, the soluble organic semiconductor materials were chosen for this project. Besides that, all experiments to fabricate thin films and MOM diode were conducted in a controlled environment by minimizing the exposure of the fabricated diode with ambient environment. The DC and AC measurement setup is required to conduct electrical and frequency-dependent impedance of MOM diodes.

1.5 Thesis Outline

The thesis contains five chapters. Chapter 1 is an introduction that gives a brief explanation of the technology that organic semiconductor, diode, transistor, and what is the limitation in achieving high efficiency organic diode. The research aim, objective scope of this thesis is presented in this chapter.

Chapter 2 is gives a brief explanation about the basic theory behind organic semiconductor. A brief review on previous research is written to show the various materials that are used for the development of organic devices.

Experimental steps are explained in chapter 3. This chapter explains the details on pre- and post-processing procedures and steps in order to form a thin film or layer and fabricate the MOM devices. A physical characterization method of determining thin film properties such as X-Ray diffraction and profilometer is also briefly explained, while experimental setup for the DC and AC measurement using an LCR meter and computer-controlled current-voltage measurement were also explained to determine the electrical properties of MOM devices.

Chapter 4 focusing on the results that obtains from the experiment. The characterization has been selected which is the frequency dependent electrical characteristics and the DC current-voltage (I-V) characteristics of the diode device.

Chapter 5 presenting the summary of the findings, conclusion and also recommendation. All the result of this work is summarized. By the thesis data, a future work regarding the thin film performance is described.