PHYSICAL AND ELECTRICAL STUDY OF ALOE VERA DIELECTRIC LAYER

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PHYSICAL AND ELECTRICAL STUDY OF ALOE VERA DIELECTRIC LAYER

by

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LIST OF ABBREVIATIONS

AFM	:	Atomic Force Microscopy
LCR	:	Inductance-Capacitance-Resistance
SEM	:	Scanning Electron Microscopy
UV-Vis	:	Ultraviolet-Visible Spectroscopy
FTIR	:	Fourier Transform Infrared
TGA	:	Thermogravimetric Analysis
SPA	:	Semiconductor Parameter Analyzer
I-V	:	Current-Voltage
J-V	:	Leakage Current Density – Voltage
C-V	:	Capacitance-Voltage
MIM	:	Metal-Insulator-Metal
OFET	:	Organic Field-Effect Transistor
OLED	:	Organic Light-emitting device
OSC	:	Organic Solar Cell
OTFT	:	Organic Thin Film Transistor
NPs	:	Nanoparticles
CAV	:	Commercial Aloe Vera
NAV	:	Natural Aloe Vera
PVP	:	Poly(4-vinylphenol)
CP	:	Cyanoethyl Pullulan
CPVA	:	Cyanoethyl Polyvinylalcohol
PMMA	:	Poly(methylmethacrylate)
PVA	:	Poly(vinly alcohol)
BCB	:	Benzocyclobutene

LIST OF SYMBOLS

ε_o	:	Permittivity of free space (F m^{-1})
C_{60}	:	Fullerene
C	:	Capacitance (pF)
Al	:	Aluminum
SiO_2	:	Silicon Dioxides
t	:	Thickness (mm)
I	:	Current (A)
J	:	Leakage current density (A/cm^2)
V	:	Voltage (V)
V_G	:	Gate voltage (V)
V_{th}	:	Threshold voltage (V)
V_D	:	Drain voltage (V)
μ_{eff}	:	Effective mobility (cm^2/Vs)
$I_{on/off}$	:	On/Off current ratio
S	:	Sub-threshold swing (V/decade)
κ	:	Dielectric constant

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KAJIAN FIZIKAL DAN ELEKTRIK LAPISAN DIELEKTRIK DARIPADA LIDAH BUAYA

ABSTRAK

Gel lidah buaya sedia ada dan gel lidah buaya semula jadi yang diekstrak dari pokok lidah buaya telah dibandingkan dan digunakan sebagai bahan dielektrik dalam peranti elektronik organik. Filem gel lidah buaya sedia ada dan gel lidah buaya semula jadi masing-masing dihasilkan di atas aluminium yang salut di atas substrat gelas secara cetak saring. Kedua-dua jenis filem lidah buaya dikeringkan dalam suhu bilik selama 24 jam dan seterusnya dikeringkan dalam ketuhar. Kesan suhu pengeringan (30-80 ℃), tempoh pengeringan (30-60 min), bilangan lapisan filem lidah buaya dan jarak di antara dua elektrod logam di atas filem lidah buaya sedia ada telah dikaji. Manakala kesan suhu pengeringan (30-90 ℃), tempoh pengeringan (30-180 min) dan muatan nanopartikel silikon dioksida (SiO_2 NPs) yang dicampur ke dalam lidah buaya semula jadi telah dikaji. Sifat-sifat struktur, fizikal dan elektrik sampel lidah buaya sedia ada dan lidah buaya semula jadi telah dikaji dan dibandingkan. Mikroskop daya atom, mikroskop imbasan elektron dan spektroskopi infra-merah jelmaan fourier telah digunakan untuk mengenalpasti perbezaan di antara kedua-dua jenis filem lidah buaya yang telah dikeringkan pada keadaan yang berbeza. Ia bertujuan untuk memahami sambung silang polisakarida dalam bahan-bahan kerana ia adalah satu pertimbangan yang penting untuk aplikasi dielektrik. Didapati bahawa satu lapisan filem lidah buaya yang dikeringkan dengan ketuhar (40 ℃ selama 30 min) telah menunjukkan kebocoran ketumpatan arus (J) yang terendah dan nilai J tidak dipengaruhi oleh jarak antara dua elektrod logam. Ini menunjukkan keseragaman elektrik daripada lapisan dielektrik. Sebagai

perbandingan dengan lidah buaya sedia ada, filem lidah buaya semula jadi yang dikeringkan dalam keadaan yang sama telah menunjukkan nilai J yang terendah (3.04×10^{-4} A/m^2) dan dielektrik malar tertinggi (k = 3.88). Peningkatan lanjut pada nilai J dan k telah dicatatkan, dengan lidah buaya semula jadi yang sama tetapi dengan tambahan sebanyak 1.5 wt% SiO_2 NPs. Oleh itu, lidah buaya yang mengandungi 1.5 wt% SiO_2 NPs telah digunakan sebagai filem dielektrik dalam OFET jenis-n berasas fullerence. Transistor kesan medan organik (OFET) beroperasi di bawah keadaan atmosfera menunjukkan pergerakan elektron dan voltan ambang masing-masing dengan nilai 1.110 cm^2/Vs and 0 V. Selepas dua minggu pendedahan di udara, nilai pergerakan elektron dan voltan ambang dikurangkan tetapi nilai tersebut masih memenuhi keperluan untuk aplikasi kod bar.

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ABSTRACT

Commercially available Aloe vera gel and naturally extracted Aloe vera gel were compared and used as dielectric material in organic electronic device. Commercial Aloe vera and extracted natural Aloe vera layers were formed respectively on aluminum coated glass substrate by screen-printing. Both types of Aloe vera layers were dried at room temperature for 24 hours and followed by oven drying in air. The effects of oven drying temperature (30-80^{o}C) and duration (30-60 min), number of stacking Aloe vera layers and distance in between two metal electrodes on commercial Aloe vera layer were studied. The effects of oven drying temperature (30-90^{o}C) and duration (30-180 min) as well as loading of silicon dioxide nanoparticles (SiO_2 NPs) on extracted natural Aloe vera layer were investigated. Structural, physical and electrical properties of the commercial and extracted natural Aloe vera samples were examined and compared. Atomic force microscope, scanning electron microscope, and Fourier transform infrared spectroscope were used to identify the differences between those two types of Aloe vera layers that had been dried at different conditions. It was aimed to understand the cross-linking of polysaccharides in the materials as it is an important consideration for electrical application. It found that single layer of oven dried (40 ℃ for 30 min) commercial Aloe vera demonstrated the lowest leakage current density (J) and the J value was not affected by the distance between two metal electrodes. This revealed the electrical uniformity of the dielectric layer. As compared with commercially available Aloe vera, naturally extracted Aloe vera layer dried at

similar conditions, where its commercial counterpart layer has demonstrated the lowest J value (3.04×10^{-4} A/m^2) and highest dielectric constant (k = 3.88). Further enhancement on J and k value was recorded, in similarity processed extracted natural Aloe vera but with addition of 1.5 wt% of SiO_2 NPs. Therefore, the Aloe vera with 1.5 wt% of SiO_2 NPs was employed as a gate dielectric in an n-type fullerene-based organic field-effect transistor (OFET). The OFET operated under atmospheric condition exhibited effective mobility and threshold voltage of 1.110 cm^2/Vs and 0 V, respectively. After two weeks of exposure in air, the effective mobility and threshold voltage were reduced but the values are still fulfill the requirement for electronic bar code applications.

CHAPTER 1

INTRODUCTION

1.1 Background

Organic materials have been used to fabricate active and passive region of organic electronic devices and are growing exponentially since 1974 (McGinnesset al., 1974). This is mainly due to their excellent properties, such as low processing temperature (Xu et al., 2011), low production cost (Shim et al., 2003), and ease of processing technique that suitable for large scale fabrication (Shim et al., 2003). With these advantages, organic materials have demonstrated their capability to be used in organic field-effect transistor (OFET) (Someya et al., 2005), organic light-emitting device (OLED) (Yan et al., 2005), organic solar cell (OSC) (Puigdollers et al., 2005), photovoltaic cell (Toda et al., 2007), sensor, and memory device (Chou et al., 2008).

Recently, in organic electronic devices, such as OFET, interest has focused on the benchmark of n-type OFET, which is based on fullerenes (C_{60}) acting as an active semiconducting layer with the highest reported mobility up to 6 cm^2/Vs (Ullah et al., 2009). Hence, it is highly desirable to achieve high-performance n-type OFETs with large electron mobility, low threshold voltage and large on/off current ratio, and that can be processed at room temperature using easy fabrication process. However not only semiconductor layer can be replaced by organic material but dielectric layer can also be replaced by organic material to form a good insulating layer (Zhang et al., 2009). Several organic materials have been investigated as the

dielectric layer, namely poly(4-vinyl phenol) (PVP) (Jiang et al., 2010), cyanoethylated pullulan (CP) (Xu et al., 2009), polystyrene (PS) (Prime et al., 2010), polyimide (PI) (Narayanan Unni, et al., 2008), benzocyclobutene (BCB), poly(vinly alcohol) (PVA) (Jang et al., 2005), parylene, poly(methylmethacrylate) (PMMA) (Xu et al., 2011), and Cytop (Li et al., 2012; Li et al., 2012). The device performance may be influenced by the type of organic dielectric being used. Therefore, selection of the dielectric material has become one of the important criteria in designing an OFET (Wang et al., 1995). However, most of the organic dielectrics are based on organic synthetic polymeric materials, there are not much study conducted on natural, organic, and environmental friendly materials. The use of organic synthetic polymeric materials have resulted significant increment in electronic waste (e-waste). (Farrow, 2006; Glowacki et al., 2012; vanLoon et al., 2010). It has estimated that up to 40 million tons of e-waste, worldwide, have been generated annually (UNEP, 2009), which severely contributed to the environmental pollution and health issues (Farrow, 2006; Glowacki et al., 2012). Therefore, utilization of environmental friendly material is of extremely important (Glowacki et al., 2012). This category of material usually refers to natural occurring materials those origin from plant, animal or living organism as they are having good end-life recyclability ("A review of national resource strategies and research," 2012) and sustainability (vanLoon et al., 2010; Kordel, Dassenakis et al., 1997). In general, natural material displays poor electrical conductivity; hence it is suitable to be used as insulator (or dielectric) in organic electronic applications (Farrow, 2006). Leakage current of any dielectric being employed in organic electronics must not higher than 10^{-3} A/m^2 at a reasonably low applied voltage with high breakdown voltage (Jung et al., 2010).

To solve the environmental pollution and health issues, the current progress is mainly focusing in investigating natural environmental friendly dielectric material. Chang et al. (Chang et al., 2011) used chicken albumen as a dielectric layer in OFET and it revealed a higher dielectric constant than most of the organic synthetic polymeric dielectrics, making it a potential dielectric layer for OFET application. In addition, tetratetracontane presents in some medicinal plants have also been investigated to be used as a natural dielectric material (Glowacki et al., 2012). Besides, dielectric properties of fresh leaves of ficus benghalensis, ficus elastica, ficus religiosa, morus nigra, hibiscus rosa-sinensis, gossypium hirsutum (Hashmi et al., 1994), maiza leaf (Ksenzhek et al., 2004), apple, avocado, banana, cantaloupe, carrot, cucumber, grape, orange, and potato tissues (Nelson, 2005) are suggested and reported briefly. Dielectric properties of poplar and monster delicious leaves have also been reported by Helhel et al (Helhel et al., 2009). This shows the potential of utilizing natural environmental friendly material as the dielectric material in organic electronic application.

Natural based dielectric material is preferable due to their ease of solution-processablility at low temperature and low cost, if compared with organic synthetic polymer (Chang et al., 2011; IrimiaVladu et al., 2010). The requirements of a natural material to be used as a dielectric layer in an OFET are (i) high dielectric constant (~3.9) (Maliakal, 2007; Jang et al., 2005), (ii) low leakage current ($>10^{-3}$ A/m^2) (Jung et al., 2010), (iii) cheap and easy to be deposited on a substrate at low temperature (Brédas et al., 2002), (iv) environmental friendly (Chang et al., 2011),

(v) surface energy match with surface energy of semiconductor layer (<15%) (Singh et al., 2006; Sun et al., 2010).

The demands to improve the dielectric properties of a dielectric material have driven the development of synthetic polymer-inorganic nancomposites (Grabowski et al., 2013). Synthetic polymer-inorganic nanocomposites have been proposed as alternatives in an effort to significantly improve dielectric properties of the devices. Besides, the key goal for dielectric polymer nanocomposites design is to avoid failure and improve the dielectric properties of polymer (Caruso et al., 2001). The dielectric permittivity must be dramatically improved by the nanoparticles to offset any reduction in breakdown properties (Grabowski et al., 2013).

The industrial use of silicon dioxides (SiO_2) is widespread from microelectronics to nuclear technology. The excellent dielectric properties of SiO_2 are extensively used in field effect transistors (Kingon et al., 2000). Nanocrystalline SiO_2/SiO_2 nanoparticles (SiO_2 NPs) have been incorporated into a variety of synthetic polymers to obtain better dielectric, thermal, mechanical and physical properties. The inclusion of dielectric nanoparticles influenced the insulating behavior of polymers due to it wide band gap. Besides, the insulating behavior of SiO_2 and the reduction chain length lead to decreased in conductivity with increase of particle content and dielectric constant of the nanocomposite increase with the increase of SiO_2 NPs content (Dutta et al., 2006). Besides improvement of dielectric, improvement of mechanical performance of biodegradable polymer, poly-caprolactone reinforced with SiO_2 NPs (Cannillo et al., 2006) has been observed. The additional of SiO_2 into epoxy resin enhanced the thermomechanical properties

(Wang et al., 2002). The optical and electrical properties of poly(phenylenevinyene) are largely influenced by SiO_2 NPs (Ho et al., 2002). The presence of SiO_2 NPs reduce the conjugation length of poly(phenylenevinyene) and consequently lower the conductivity compared to the bare polymer. Due to the advantages of SiO_2 NPs to dielectric properties, the additional of SiO_2 NPs into natural based dielectric material is being encouraged.

1.2 Problem Statement

OFET has been developed since three decades ago (Puigdollers et al., 2005). Various types of dielectric materials have been used as insulator layer in OFET. The inorganic synthetic materials that were reported used in OFET are listed in Table 1.1.

Table 1.1 Inorganic synthetic dielectric materials used in OFET and their drawback.

Dielectric Materials	Dielectric constant	Drawback
Zirconium oxide (ZrO_2)	22.0	• Surface defects and traps (Liwei et al., 2009)
Tantalum pentoxide (Ta_2O_5)	25.0	• Lack of stability (Liwei et al., 2009) • Fail to yield flexible devices (Jiongxin et al., 2007)
Hafnium oxide (HfO_2)	25.0	• Difficult in forming smooth film on plastic (Jiongxin et al., 2007) • Fail to form flexible devices (Jiongxin et al., 2007)
Alumina (Al_2O_3)	9.8	• Difficult in forming smooth film on plastic (Jiongxin et al., 2007) • Fail to yield flexible devices (Jiongxin et al., 2007)

Other than inorganic synthetic materials, organic synthetic polymers have also been applied as dielectric layer in OFET device. Organic synthetic polymer is the dielectric material that often being used as gate dielectric layer. Examples for synthetic polymers are shown in Table 1.2.

Table 1.2 Synthetic polymer dielectric material used in OFET and their drawback.

Dielectric Materials	Dielectric constant	Drawback
Polymethymethacrylate (PMMA)	3.60	• Low capacitance due to low dielectric constant property (Liwei et al., 2009)
Polyvinyl alcohol (PVA)	4.05	• Low immunity against moisture (Abbas et al., 2011; Jang et al., 2005)
Cyanoethylated pullulan (CP)	13.00	• Low immunity against moisture (Xu et al., 2009)
Poly(α-methylstyrene) (PαMS)	2.5	• Trapped charge (Baeg et al., 2006)
Polystyrene (PS)	2.60	• Function not as good as PαMS (Baeg et al., 2006)
Polyvinylphenol (PVP)	3.50	• Higher current leakage compared to PMMA (Kang, et al., 2005)
Benzocyclobutene (BCB)	2.60	• Higher moisture taken (Gupta, 2009) • Required to post processed at relatively high annealing temperature anthopoulos (Anthopoulos et al., 2006; Th B. Singh et al., 2007)

Besides environmental pollution and health issues, the drawbacks of synthetic organic and inorganic based dielectric which are listed in Table 1.1 and 1.2, respectively. Due to drawbacks in the dielectric materials stated above, improvement is needed for better function of dielectric layer in OFET. In this research, Aloe vera

gel was used as dielectric material, which has been found that Aloe vera leaf has the ability to be dielectric material due to it weak conductivity.

Aloe vera leaf can be divided into two major parts, inner colorless Aloe vera pulp and outer epidermis layer with cuticle (Hamman, 2008). Polysaccharides have been detected from the pulp including such as monosaccharide mannan, galactan, arabinan, arabinorhamnogalactan, pectic substance and glucuronic (Miranda et al., 2010). The major polysaccharide of the pulp is mannan; mannose is a monomer of mannan and mannose only contains single chain bonds that have low mobility and do not contribute to the electrical conductivity. This makes Aloe vera pulp suitable to be used as dielectric material (Kumar et al., 2010; Miranda et al., 2010; S. Ravi et al., 2011). In addition, it has many favorable properties such as environmental friendly, solution-processable at low temperature, no chemical synthesis requires, and low in processing and producing cost. Therefore, this type of natural material is being used in this work. Besides, environmental friendly SiO_2 NPs which has been incorporated into a variety of synthetic polymers to obtain better dielectric and physical properties is loading into the Aloe vera gel to enhance the dielectric properties of Aloe vera gel.

1.3 Research Objectives

The main objective of this research is to investigate a dielectric material by using a natural environmental friendly material – Aloe vera. With this main objective, the following aspects are to be achieved:

1. To investigate the effects of drying temperature, drying duration, number of Aloe vera layer, distance between two electrodes and/or loading of SiO_2 NPs on the dielectric properties of commercially available and naturally extracted Aloe vera gel.
2. To compare the dielectric properties of the optimum commercial available and naturally extracted Aloe vera gel.
3. To test the workability of the optimum natural Aloe vera gel as a dielectric layer in C_{60}-based OFET.

1.4 Scope of Study

In this study, two different Aloe vera gels have been used as dielectric material; commercially available Aloe vera gel and naturally extracted Aloe vera gel without chemical addition. Aloe vera gel was screen-printed on aluminum (Al) coated glass substrates and then dried in room temperature for 24 hours. Various parameters were performed, namely (i) effects of drying temperature on the commercial available Aloe vera layer on Al coated glass substrate, (ii) effects of oven driedrying duration on the commercial available Aloe vera layer on Al coated glass substrate, (iii) effects of successive applying the Aloe vera layer on the Al coated glass substrate and distance in between two electrodes (source and drain), (iv) effects of drying temperature on the extracted natural Aloe vera layer on Al coated glass substrate, (v) effects of drying duration on the extracted natural Aloe vera layer on Al coated glass substrate, (vi) effects of loading of SiO_2 NPs weight percent content in the extracted natural Aloe vera layer on Al coated glass substrate with

optimized drying parameter, and (vii) application of extracted natural Aloe vera blended with 1.5 wt% of SiO_2 NPs as a dielectric layer in C_{60}-based OFET.

Structural and chemical characterizations of Aloe vera layers were conducted by using fourier transformed infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), ultraviolet-visible spectroscopy (UV-Vis), goniometer, field emission scanning electron microscopy (FE-SEM), table-top SEM, digital microscope, and atomic force microscopy (AFM). On the other hand, Semiconductor parameter analyzer (SPA), Dielectric test fixture and LCR meter were employed to characterize the electrical properties of the Aloe vera layers.

1.5 Thesis Outline

This thesis is organized and divided into five chapters. Chapter 1 provides an overview of current issues and challenges faced in dielectric material, research objectives, and scope of study. Chapter 2 covers the detailed literature review, which corresponds to the background theories adopted in the study. The following chapter 3 presents the systematic methodology of the research. Chapter 4 focuses on the results and discussion from the conducted characterizations. Chapter 5 summarizes this study and its conclusions. Recommendations for future works are also presented in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The first organic electronic device was reported in 1974 (McGinness et al., 1974). In 1987, the first OFET based on polymer of thiophene molecules was reported by Koezuka and co-workers. In the same year, OLED was first developed at Eastman Kodak Company by Tang and VanSlyke (Tang et al., 1987). Recent years, organic materials have been widely used in fabricating electronic devices due to their ease of processing at low temperatures, low fabrication cost and environment friendly due to increasing of e-waste annually (Maliakal, 2007; Chang, et al., 2009; G.Lu, 2006; Puigdollers et al., 2005; Veres al., 2004; Xu et al., 2011).

Although organic materials have been employed as the active layer in OLED (Chou & Cheng, 2008), OFET (Horowitz, 1998), organic thin film transistor (OTFT) (Huang et al., 2007; Chou et al., 2008), memory device, sensors, and organic solar cell (Chou et al., 2008), but this thesis only focuses on the application of OFET. Much attention has been paid on organic semiconductor layer used in OFET (de Boer et al., 2004). Recently, there are increasing works on the research related with organic dielectric layer (Chiu et al., 2011; Choi et al., 2009). Inorganic dielectric has less interest in OFET due to its limitation in particular needs of higher threshold voltage to turn on the device (Ponce Ortiz et al., 2010). Threshold voltage is inversely proportional to capacitance of a dielectric in OFET. According to Niinistö *et al.* (Niinistö et al., 2004), inorganic dielectric material, which has dielectric

constant (k) higher than the k value of SiO_2 (k = 3.9), is termed as high-k material. By using high-k material with a thick layer, leakage current through the layer can be minimized (Gusev et al., 2001). However, it may affect the threshold voltage as the voltage is directly proportional to the thickness of the dielectric layer (Gusev et al., 2001; Ponce Ortiz et al., 2010). With high threshold voltage, it may reduce lifetimes of the OFET (Lo et al., 1997; Ponce Ortiz et al., 2010). In order to reduce the threshold voltage, a thinner dielectric layer with lower k value is needed (Groner et al., 2003). Organic dielectric, therefore, conforms to these requirements as in general, the dielectric constant of organic dielectric is lower than of inorganic dielectric (Ponce Ortiz et al., 2010; Yang et al., 2006). Organic dielectrics have been used for OFETs including PMMA, PVA, PVP (Kim et al., 2008; Mukherjee et al., 2010; Narayanan Unni et al., 2008), polyimide (Narayanan Unni et al., 2008), teflon (PTFE) (O'Connor et al., 2009), polyvinylidene fluoride (PVDF), cyano resin (Chandar Shekar et al., 2004), BCB (Unni et al., 2004), Cytop (Li et al., 2012), and CP (Narayanan Unni et al., 2008). However, due to the increment in electronic waste (e-waste), such as synthetic polymeric materials, have contributed to environmental pollution and health issues (Farrow, 2006; Glowacki et al., 2012; Jung et al., 2010; UNEP, 2009; vanLoon et al., 2010; Kordel et al., 1997). Therefore, utilization of environmental friendly materials is important. Chang et al. (Chang et al., 2011) used chicken albumen as a dielectric layer in OFET and it revealed a higher k than most of the synthetic polymeric dielectrics, making it a potential organic dielectric layer for this application. In addition, tetratetracontane presents in some medicinal plants have also been investigated to be used as a natural organic dielectric material (Glowacki et al., 2012). Besides, capacitance and conductance of fresh leaves of ficus benghalensis, ficus elastica, ficus religiosa, morus nigra,

hibiscus rosa-sinensis, and gossypium hirsutum have been analyzed by using dielectric spectroscopy (Glowacki et al., 2012). Resistance values of maiza leaf was measured directly on the fresh leave by impendence analyzer (Ksenzhek et al., 2004). Permittivity of apple, avocado, banana, cantaloupe, carrot, cucumber, grape, orange, and potato tissues (Nelson, 2005) were obtained directly from the cutter part from the samples by impedance analyzer and reported briefly. Permittivity of poplar and monster delicious leaves have also been measured directly by using Gunn oscillator (Helhel et al., 2009).

In addition, dielectric material deposition techniques are crucial to determine the properties of the respective dielectric. Deposition techniques which have been reported are spin coating (Abbas et al., 2011; Ukah et al., 2011), vapor deposition (Narayanan Unni et al., 2008), screen printing (Janos Veres et al., 2004), plasma polymerized (Lim et al., 2010), vacuum processing process (Kanbur et al., 2012), gravure printing (de la Fuente Vornbrock et al., 2010; Park et al., 2010), ink jet printing (Park et al., 2010), laser thermal transfer printing (Ling et al., 2004), roll-to-roll printing (Choi et al., 2012; Kushida et al., 2011), stamping, microcontact printing, micromolding (Bao, 2000), flexography (de la Fuente Vornbrock et al., 2010), and nanoimprint technique (Cui et al., 2008; Hsiung et al., 2009).

Dielectric layer can influence the OFETs performance in many ways. Therefore, it is important to fully understand the various factors that affect the performance of OFET. Review related to organic dielectric layer is mainly incorporated into a major review of architecture (Janos Veres et al., 2004) and operational of OFET (Dhar et al., 2011), organic semiconductor layer (de Boer et al.,

2004) and inorganic dielectric layer used in OFET (Ponce Ortiz et al., 2010) until year 2012. Therefore, inhere; the development of organic dielectric layers used in OFETs will be reviewed. Besides, the important factors of organic dielectric layer that are influencing the performance of the OFET will be reviewed as well.

2.2 Organic Field-Effect Transistor (OFET)

OFETs have attracted attention due to their ease of solution-processability at low temperature and low cost (Maliakal, 2007; Chang et al., 2009; Shea et al., 2005; Janos Veres et al., 2004; Xu et al., 2011). With these advantages, OFETs play an important role in applications such as electronic bar codes or active matrix elements for displays with minimum required effective mobility of 0.1 to 0.5 cm^2/Vs (James et al., 2012a; Li et al., 2011; O'Neill et al., 2012) and gate voltage in range of 20 to 80 V, which is higher than the threshold voltage of an OFET (Kuribara et al., 2012). Threshold voltage reflects the minimum gate voltage applied to make the charge to mobile in OFET (Fornari, 2011), i.e., threshold voltage are in range of 3 – 15 V (DEIF, 2013; Sony, 2010), and threshold voltage close to zero is generally advantageous since large gate voltage is not required to switch on the device (James et al., 2012). Recently, interest has been focused on the benchmark of n-type OFET, which is based on C_{60} acting as an active semiconducting layer with the highest reported mobility up to 6 cm^2/Vs (Ullah et al., 2009). The gate voltage and threshold voltage of the n-type OFETs are not only affected by the properties of semiconductor and dielectric layer, which is also depending on the deposition technique, condition, treatment and choice of electrodes (gate, source, and drain) material, interface between electrodes and semiconductor or dielectric layers

(Fornari, 2011; Lee et al., 2012; Sangeeth et al., 2010). In addition, mobility of the n-type OFETs is strongly depends on the gate dielectric material, deposition methods of semiconductor and dielectric layers and interface between semiconductor and dielectric layers (Li et al., 2011).

n-type OFET based on C_{60} is usually coupled with conventional synthetic dielectric materials, namely, BCB (Matt et al., 2006), aluminum oxide/BCB (Al_2O_3/BCB) (Zhang et al., 2008), parylene-C (Nigam et al., 2012), tantalum pentoxide (Ta_2O_5) (Ueno et al., 2005), Al_2O_3 (Itaka et al., 2006), polyvinyltoluene (PVT) (Abbas et al., 2011), SiO_2/zirconium-silicon oxide/ SiO_2 (SiO_2/ZSO/SiO_2) (Kitamura et al., 2007), SiO_2/PMMA (Feng et al., 2011), PI (Kubozono et al., 2005), and SiO_2 (Matsushima et al., 2007). The reported mobility values of these OFETs are in the range of 6.6 x 10^{-7} to 6.0 cm^2/Vs. The synthetic dielectrics mentioned above are deposited by spin coating with post thermal cured (Matt et al., 2006), atomic layer deposition with post thermal cured (Zhang et al., 2008), vapor evaporating (Nigam et al., 2012), thermal growth (Konishi et al., 2008; Schwabegger et al., 2011), and thermal evaporation (Itaka et al., 2006) techniques. While C_{60} is deposited on those synthetic dielectric layer using hot wall epitaxy (HWE) (Matt et al., 2006), vacuum vapor deposition (Kitamura et al., 2007; Olthof et al., 2012), molecular beam deposition (Ueno et al., 2005), thermally evaporation (Kubozono et al., 2005), drop casting (Kang et al., 2011), and spin coating (Wöbkenberg et al., 2008) techniques. Although hot-wall epitaxy deposited C_{60} on BCB synthetic dielectric revealed the highest mobility (6 cm^2/Vs), the technique employed to produce the BCB and C_{60} layer is suffering some disadvantages. The BCB layer on ITO/glass substrate is required to post processed at relatively high

annealing temperature (250°C for at least 30 min with Ar gas or for 2 h in vacuum oven) and BCB has to heat to 300 or 250°C during deposition of C_{60} (Singh et al., 2005). The processing conditions of BCB and C_{60} are strongly influencing mobility of the OFET (Anthopoulos et al., 2006; Singh et al., 2007; You et al., 2000). Therefore, dielectric materials that are solution-processable at low temperatures must be developed in order to replace the conventional synthetic dielectric materials that need high deposition temperature and/or post-deposition process (Horowitz, 1998; Singh et al., 2006). Thus, there is growing interest in developing n-type OFET based on C_{60} with natural dielectric because of its low cost, solution deposition and low temperature process. Chang et al. (Chang et al., 2011) developed the OFET with chicken albumen as the natural dielectric and cured at 80 to 140°C, which is deposited by spin coating technique has exhibited a mobility of 0.13 cm^2/Vs.

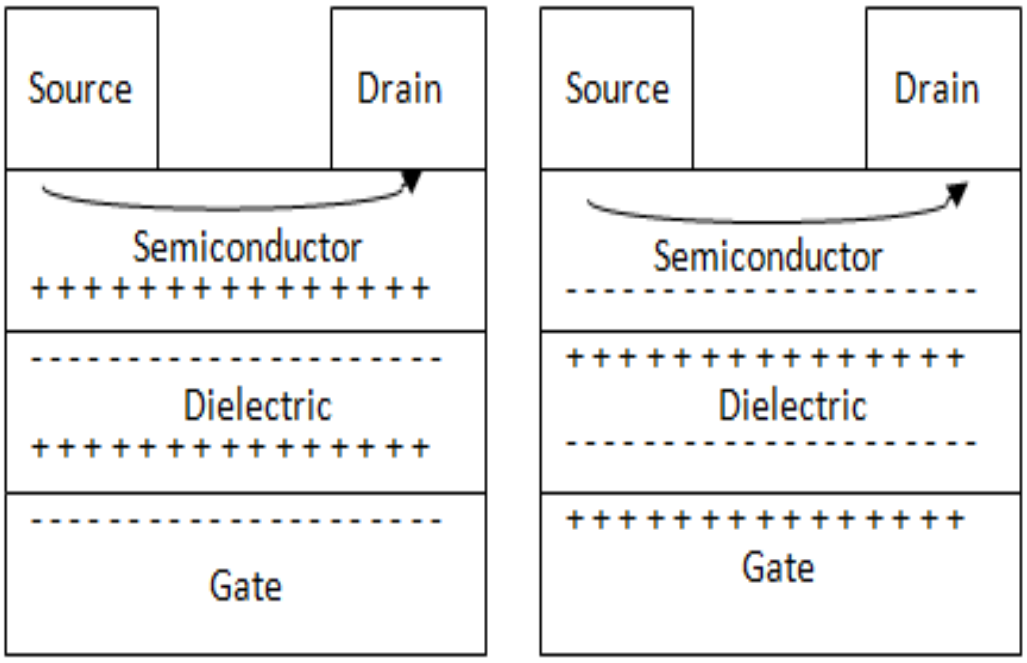
2.2.1 Operation of OFET

The transistors based on organic semiconductors as the active layer to control the current flow are commonly referred as OFETs (Horowitz, 1998). In OFETs, the steps of operation involve charge injection and formation of a conducting channel within the organic semiconductor is governed by two independent voltages perpendicular to each other (Li et al., 2011). The role of gate voltage (V_G) is to induce charges in the conducting channel, while drain voltage (V_D) drives these charges from source to drain electrode (Li et al., 2011). OFET can be classified by either as n-type or p-type OFET (Horowitz, 1998). For n-type OFET, a positive voltage applied to gate electrode and set up a conduction channel that induces negative charge carrier (electron) to accumulate in the semiconductor near

dielectric and semiconductor interface (Li et al., 2011). This accumulation layer forms a conducting channel in semiconductor, allowing charge carriers to be driven from source to drain by applying a positive voltage to the drain electrode (Li et al., 2011) (Figure 2.1). The effective mobility can be calculated from the linear or saturation region using Eq. 2.1 and 2.2, respectively (Li et al., 2011).

$$I_D = (W/L)\ \mu C\ [V_G - V_T - (V_D/2)]\ V_D \quad (2.1)$$

$$I_D = 1/2\ (W/L)\ \mu C\ (V_G - V_T)^2 \quad (2.2)$$



(a) (b)

Figure 2.1: Simplified illustration of the operation of (a) p-type OFET and (b) n-type OFET (Li et al., 2011).

2.3 Structure of OFET

The basic components of an OFET are shown in Figure 2.2. It consists of an organic-based semiconductor, three electrodes (gate, source and drain), a dielectric layer, and a supporting substrate. The space between source and drain is a channel, with a length (L), and a width (W) (Yamao, Ota, Miki, Hotta, & Azumi, 2008). The source and drain contact directly with semiconductor layer while the gate electrode is separated from semiconductor layer by a dielectric layer with thickness d (Charrier, 2009). The operation of an OFET depends on thickness of dielectric layer and channel length between source and drain (Paasch, Scheinert, & Tecklenburg, 1997). The basic components can be arranged and formed into four OFET structures (Figure 2.3) (Nenad et al., 2011). All of these structures are formed on top of a supporting substrate. In the following sub-sections, each individual component will be explained in brief while organic dielectric layer will be reviewed in particular.

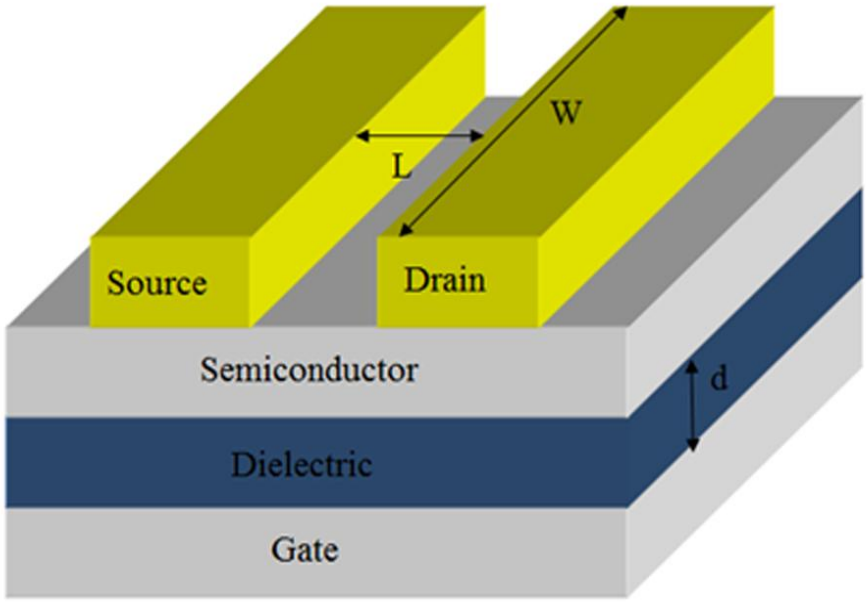


Figure 2.2: Structure of an OFET (Yamao et al., 2008).

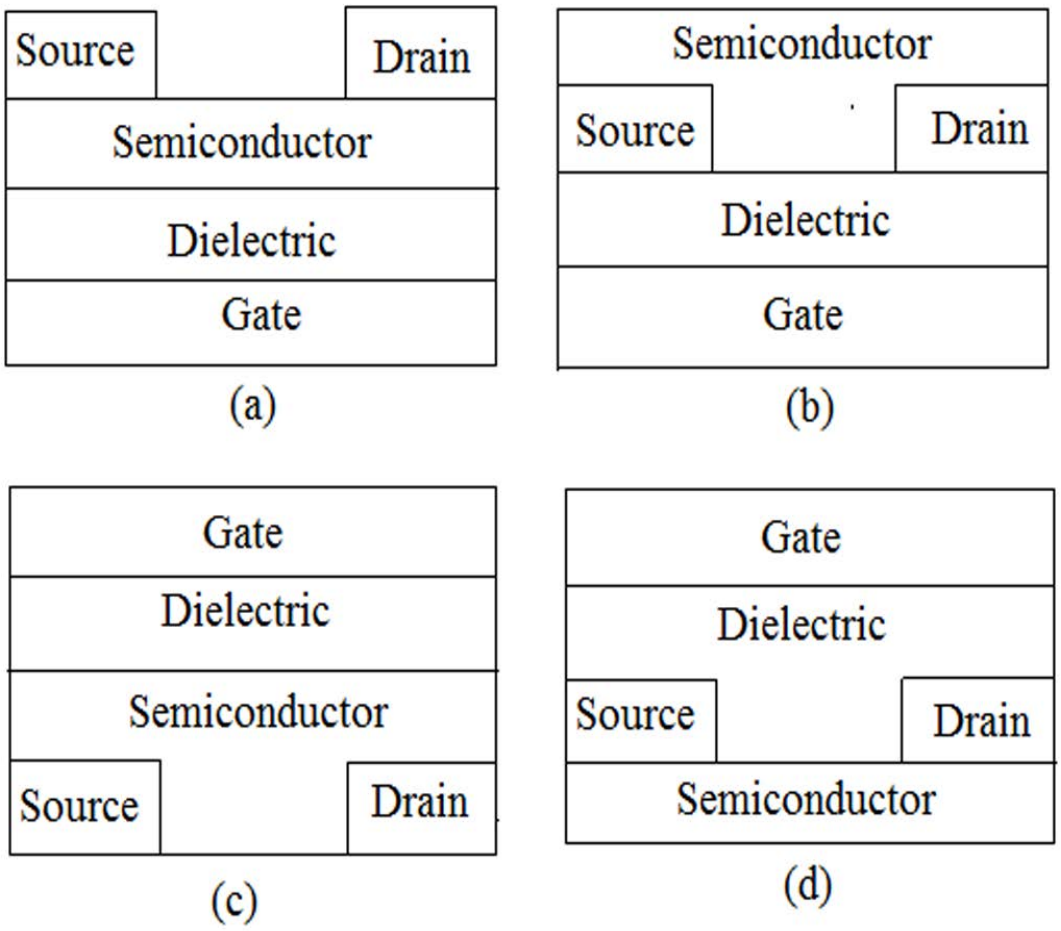


Figure 2.3: Typical structures of OFET (a) Bottom-gate top-contact, (b) Bottom-gate bottom-contact, (c) Top-gate bottom-contact, (d) Top-gate top-contact (Ling et al., 2004; Ponce Ortiz et al., 2010; Singh et al., 2006).

2.3.1 Substrates

Substrate is a base that functions as mechanical support of an OFET device. Quartz, polyethylene (Chandar Shekar et al., 2004), glass (Abbas et al., 2011), silicon (Choi et al., 2008), indium tin oxide (ITO) coated glass (Lim et al., 2010), and polyimide (Jiang et al., 2010; Sekitani et al., 2011) are synthetic substrates in an OFET. Besides, natural materials, such as ecoflex, caramelized glucose, and hard

gelatin, are also being used as a substrate (IrimiaVladu et al., 2010). Selection of these substrate materials is important as it may directly affect the functional area and applications of the OFET. Besides, surface flatness, roughness and cleanness of a substrate play a vital role which affect the quality of dielectric or semiconductor layer deposited on top of it (Chen et al., 2006; Jiang et al., 2010; Lee et al., 2009; Lim et al., 2010; Narayanan Unni et al., 2008; Noh et al., 2009; Ukah et al., 2011). Therefore, substrate cleaning process is essential and it is a material-type-dependent-process. Typically, glass and flexible polymer substrates are cleaned by ethanol, acetone, or 2-propanol, and de-ionized water in ultrasonic bath (Ainsebaa et al., 2011; Prime et al., 2010; Wei et al., 2011). For inorganic substrates, such as quartz and silicon wafer are cleaned by piranha solution cleaning process and hydrofluoric acid solution (Shehu et al., 2010; Zan et al., 2009). These processes are used to remove the organic residues and native oxide layer on the substrates (Zan et al., 2009).

2.3.2 Electrodes

Usually, metal is used to fabricate gate, source and drain electrodes due to its excellent electrical property compared with other materials, such as ceramic and polymer. The electrical property of metals affect the electrical performance of an OFET, in particular the charge carrier mobility (Valletta et al., 2011). The utilization of platinum (Pt) (Chandar Shekar et al., 2004; Toda et al., 2007), palladium (Pd) (Chandar Shekar et al., 2004), copper (Cu) (Liu et al., 2011), aluminum (Al) (Abbas et al., 2011), gold (Au) (Park et al., 2010; Qiu et al., 2003), silver (Ag) (Jiang et al., 2010), calcium (Ca) (Abbas et al., 2011; Chang et al., 2010), and chromium (Cr)

(Toda et al., 2007) as electrodes of an OFET have been reported. Depending on the work function of electrodes, interaction of electrodes with semiconductor layer may influence their contact resistance (Chu et al., 2005; Park et al., 2010; Whiting et al., 2009; Yasuda et al., 2005). Therefore, barrier height between electrodes and semiconductor is an important parameter. To form an ohmic contact, a low resistance junction provides current conduction from semiconductor to metal and vice versa, the barrier height must be as low as possible which the work function of metal to match with highest occupied molecular orbital (HOMO) of the organic semiconductor in p-type OFET, and with the lowest unoccupied molecular orbital (LUMO) in the case of an n-type OFET (Li et al., 2011). For n-type OFET, metal with low work function, such as Ca (2.9 eV) , Al (4.08 eV) (Mechtly, 2002), are selected as source and drain electrodes because of their work functions which are well matched with the LUMO energy level of n-type organic semiconductor (Hong et al., 2011). This leads to a lower electron injection barrier between electrodes and semiconductor layer [Figure 2.4(a)] (Hong et al., 2011; Manaka et al., 2009). For p-type OFET, higher work function value is preferable, for example, Au (5.1 eV) is used because its work function matches with the HOMO of p-type organic semiconductor (Manaka et al., 2009) [Figure 2.4(b)]. Besides, the physical matching of two materials of both electrodes and semiconductor layer is important, because it influences the interface layer formed between electrodes and semiconductor layer. This interface layer may interfere with the carrier transport through electrodes and semiconductor layer which effect's the electrical performance of an OFET (Vilan et al., 2002).

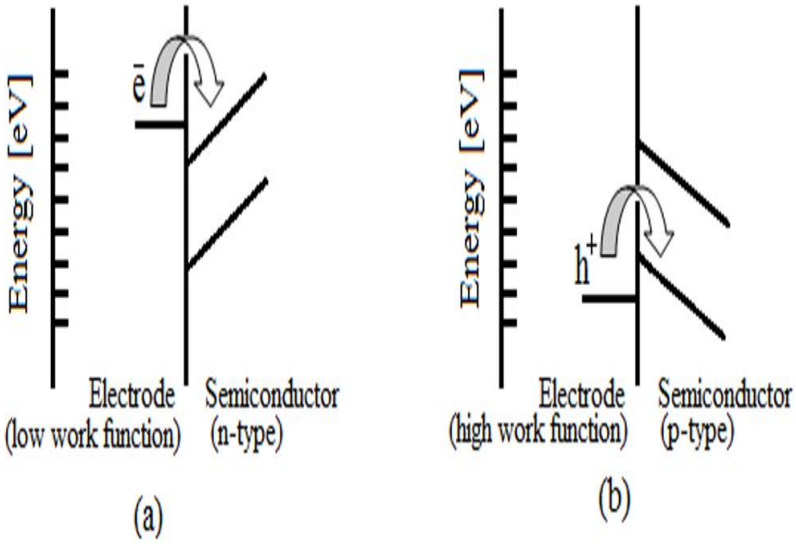


Figure 2.4: Structure with the energy levels of the contact-semiconductor materials where charges take place (Antonio Facchetti, 2010).

In addition, position of source and drain electrodes, either as top-contact or as bottom-contact may also influence the performance of OFET (Chang et al., 2010). For top-contact bottom-gate structure, the source and drain electrodes are deposited on the top of the organic semiconductor layer (Streer et al., 2002). This structure has larger contact area between the source/drain electrodes and semiconductor layer (Figure 2.5a) and the charge injected from electrodes into organic semiconductor is more effective (Streer et al., 2002), if compared with the bottom-contact bottom-gate structure (Figure 2.5b) (Li et al., 2011). This is because presence of source and drain electrodes, i.e., bottom-contact may affect molecules arrangement in organic semiconductor during deposition of semiconductor layer process (Kymissis, 2009). During semiconductor deposition, semiconductor molecules may land on dielectric layer with higher polarizability edge-on molecules ordering to obtain minimum potential energy configuration [Figure 2.5(c)] (Kymissis, 2009). Edge-on molecules

ordering are having strong stacking π-π interaction between each others, as a result charge transport between electrodes and organic semiconductor become more effective. However, for bottom-contact structure which the semiconductor molecules are deposited on source and drain electrodes, the semiconductor molecules electron cloud are facing flat into the electrode layer to obtain lowest potential energy configuration with the maximum polarizability (Braga et al., 2009). The organic semiconductor molecules laid on source and drain electrodes have different configurations compared with those laid on dielectric layer (Kymissis, 2009) [Figure 2.5(d)]. This inconsistent growth pattern along the edges of the electrodes will lead to higher density of traps between semiconductor layer and electrodes interface. Consequently, resistance of electrodes is increased and it makes the transportation of charge carrier more difficult (Braga et al., 2009). However, damage and degradation in organic semiconductor layer occur whenever metal electrodes are deposited on semiconductor layer (Streer et al., 2002). It is due to high temperature is required for source and drain electrodes deposition process (Ling et al., 2004).

In addition, the source and drain electrodes of top-contact structure are fabricated by using shadow-mask technique (Nurul et al., 2009) in which larger distance is created between two electrodes. This causes a lower mobility of charge carrier (Rhee et al., 2008). Thus this design is not frequently used (Streer et al., 2002) and mainly used to fabricate long channel length devices. For bottom-contact structure, standard lithographic technique can be used to fabricate short channel length devices that can achieve a higher mobility of charge carrier (Lee et al., 2005; Li et al., 2006; Ling et al., 2004; Nurul et al., 2009). This lithographic technique is not suitable to be applied on top-contact structure because photoresists procedure

may damage the semiconductor layer as a result of either chemical degradation or change of film morphology (Ling et al., 2004). Since, due to the pros and cons of bottom and top-contact structure, careful consideration is required when designing a fabrication procedure for OFET.

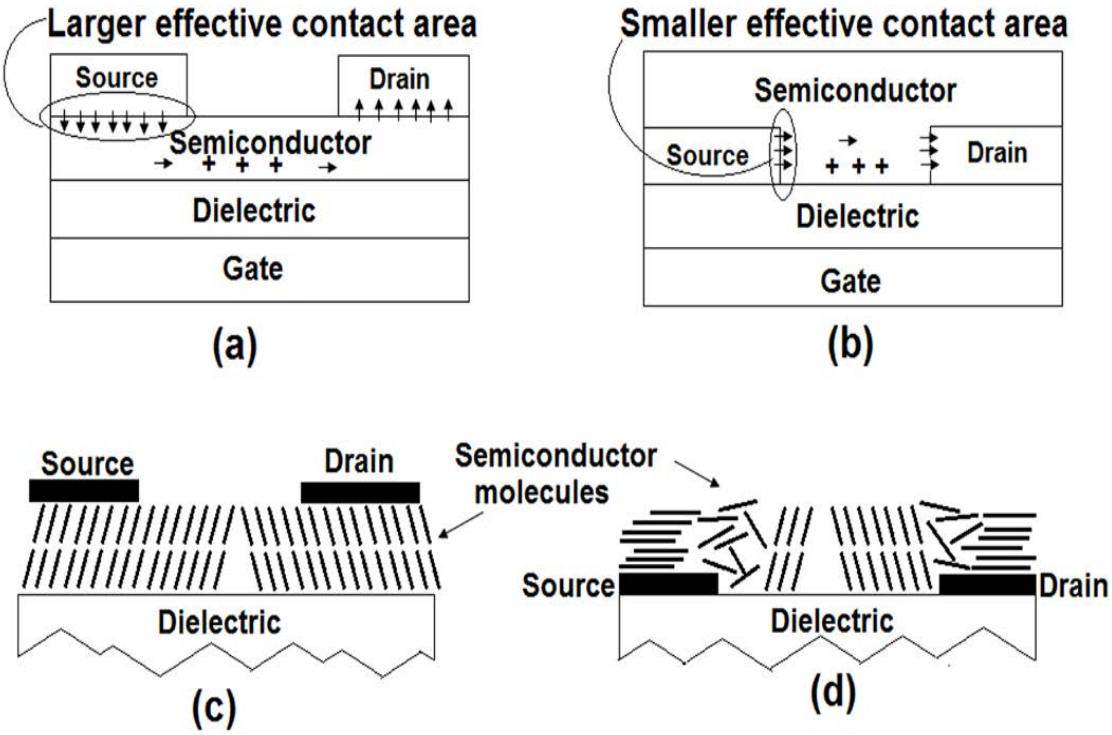


Figure 2.5: Cross-section of bottom-gate configuration for (a) top-contact electrical characteristic, (b) bottom-contact electrical characteristic, molecular packing in (c) top-contact and (d) bottom-contact OFET (Kymissis, 2009; Li et al., 2011).

2.3.3 Organic Semiconductor Layer

Organic semiconductor is classified as n-type or p-type. The majority carriers in both n-type and p-type semiconductors are electrons and holes,

respectively (Sun et al., 2005). So far most works are focused on p-type organic semiconductors, such as pentacene, due to their good stability in air and superior charge carrier mobility (> 1 $cm^2V^{-1}s^{-1}$) (Chang et al., 2009; Chen et al., 2006; Shaw et al., 2001; Schön et al., 2000; Wei et al., 2011). On the contrary, most n-type semiconductors have relatively low charge carrier mobility. They are susceptible to air and moisture which cause them not suitable to be used at open air environment (Sun et al., 2005). Organic semiconductor, with π bonding as its backbones, is widely used in OFET as the active layer (Chason et al., 2005; Antonio Facchetti, 2010). The π bond between organic molecules acts as a pathway for charge carrier transport via hopping process (Bao, 2000; Chason et al., 2005; Antonio Facchetti, 2010). Therefore, individual molecule orientation and its structure ordering strongly influence the performance of OFET (Bassler et al., 2012; Horowitz, 1998; Kola et al., 2012; Pron et al., 2001; Sun et al., 2005; Ueno, 2012). The reduction of π bandwidth or distance between molecules may enhance the hopping process (Brédas et al., 2002; Stallinga, 2009; Sun et al., 2005). This can be achieved by applying an external heat to the semiconductor, choosing the suitable organic materials, controlling parameters during deposition process conditions and utilizing compatible fabrication technique (Brédas et al., 2002; Chang et al., 2004; Chason et al., 2005; Jurchescu et al., 2004; Kola et al., 2012; Lin et al., 1997; Sun et al., 2005).

Besides, charge carrier transportation in OFET is affected by the imperfections located either in organic semiconductor layer or on the interface between organic semiconductor layer and dielectric layer (Antonio Facchetti, 2009; Lin et al., 1997; Zhang et al., 2009). The imperfection of organic semiconductor layer is associated closely with the purity of respective organic semiconductor