Solution-Processed Conducting Films for Organic Field-Effect Transistors (OFETs)

A thesis submitted to The University of Manchester for the degree of Master of Philosophy in the Faculty of Engineering and Physical Sciences.

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Abstract

Transparent conducting materials are widely used as contact electrodes in optoelectronic applications such as liquid crystal displays (LCDs), solar cells, light emitting diodes (LEDs) and Thin Film Transistors (TFTs). Future bendable optoelectronic devices will require suitable fabrication methods for flexible transparent electrodes to be formed at low cost on large areas. The most used materials among these applications, are doped metal oxides (mainly indium tin oxide, ITO) because of their high electrical conductivity and high optical transparency. However, doped metal oxides have many disadvantages: they are expensive, some require high vacuum during thin film fabrication processes and are prone to cracking on flexible substrates. Alternatives to Indium Tin Oxide (ITO) have been developed in recent years to replace it.

The aim of this project was to develop novel organic-inorganic nanocomposite materials that combine high conductivity and transparency intrinsic to doped semiconducting metal oxides with low-cost and ease of processing characteristic for polymers that will pave the way towards low cost fabrication and integration of transparent conducting materials for high performance electronic components (e.g. Thin Film Transistors, Photovoltaic cells, Light Emitting Diodes) and circuits on flexible substrates. This involved formulation of polymer/nanowire nanocomposite solutions, as well as fabrication and electrical characterisation of thin conductive films and Organic Field-Effect Transistors (OFETs) for applications such as driving circuits for displays and sensors that require low switching speed, as well as low voltage and power operation.

In this work, solution-processed silver nanowire (AgNW) electrodes to be used as transparent contacts for thin film transistors have been developed by demonstrating low sheet resistance and high transmittance. The performance of the electrodes depends on the properties of the silver nanowires (AgNWs), their roughness, as well as thin film sheet resistance and transparency. A transparent insulating polymer (polyvinyl alcohol, PVA) was used as both a high-k dielectric ($k = 7.8$) and as the top layer of the silver nanowire electrodes to form a composite during the fabrication of Organic Field-Effect Transistors (OFETs). It is shown that using this approach, low threshold voltage Organic Field-Effect Transistors (OFETs) operating with gate voltages $|V_G| \leq 5$ V can be successfully realized.

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Chapter 1

1. Introduction

1.1. Background

Over the last decade there has been a massive increase in the sales of optoelectronic devices such as touch screens, electronic paper, liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and solar cells [1]. Consequently, there is a huge demand for transparent electrodes since this is an essential component of such devices.

The abundance of optical and electronic properties such as high electrical conductivity and high optical transparency that transparent electrodes possess has attracted an enormous interest from the electronic industry and stirred significant research activities towards a vast number of applications in optoelectronic devices and producing invisible electronic circuitry.

Recently, electronic devices based on organic semiconductors, such as organic field-effect transistors (OFETs) and organic light emitting diodes (OLEDs) have attracted much interest as possible inexpensive and flexible alternatives to inorganic devices. Despite considerable improvement in device properties, a better understanding of the nature of charge transport in these devices and the physics of contacts are crucial to further development of optoelectronic organic devices.

Organic, as well as many thin film inorganic optoelectronic devices, all require a transparent electrode to allow light to enter or leave the device while conducting charge across its surface. This film must be highly transparent, have a low sheet resistance and be compatible with high-quality device manufacture.

Ideally, the fabrication of the transparent thin films that permit one to bring electrical currents or potentials in the proximity of optically active regions without significant loss of optical energy via a cheap solution processed manner is required on flexible substrates, at the same time delivering device characteristics of good quality [5][2].

Liquid crystal display (LCD) is presently the largest user of transparent conductive materials but there is a growing demand for other devices such as touch panels for use in smartphones and tablets in relation to the characteristics of the transparent conductive thin film that is used in the user interface [3]. In 2012, the Touch Panel Transparent Conductive Film (TCF) market was $956 million, and markets are anticipated to reach $4.8 billion by 2019, while today the global transparent conductive film market size is estimated to be USD 4.5 billion in 2020 and is expected to reach USD 10.2 Billion by 2028. Hecht *et al.* reports that they stated e-Paper is projected to have a 30 fold increase in growth from the year 2008 to 2014, thin film solar cells will have projected sales of over $13 billion by the year 2017, and organic light emitting diodes (OLEDs) has made decent progress over the years and there is also a demand for flexible films in the market to reduce weight, space, assembly cost or even make them wearable, stretchable, and compatible with large scale manufacturing methods because currently these devices are typically found on rigid substrates such as glass. This rapid development is forecast to continue with demand; [3] therefore there is a requirement for the advancement of consumer electronics and the improvement of their properties [4].

Indium tin oxide is currently used as a Transparent Conducting Film (TCF) in the above-mentioned electronic devices because of its exceptional optoelectronic properties but there are more than a few limitations to this material. Due to its rising demand, and the anticipated shortage of indium resources, it is becoming expensive. Indium Tin Oxide (ITO) cracks easily thereby restraining its use for flexible electronics and lastly Indium Tin Oxide diffuses into the active layers of Organic Photovoltaic cells (OPVs) or Organic Light Emitting Diodes (OLEDs) resulting in poor device performance [5]. There is also the challenge of exploiting the electronic and optical properties of such materials to their greatest expectations without compromising the other. Thicker films of Indium Tin Oxide (ITO) result in higher conductivities but as a result lead to lower device transparency and heavy weight devices [1].

Replacement of Indium Tin Oxide (ITO) films with alternative materials that have similar optoelectronic properties are therefore needed particularly in the electronics sector to keep up with demand and the trend of device development soon. Alternative materials include conducting polymers such as poly (3, 4-ethylenedioxythiophene) poly (styrene sulfonate) (PEDOT: PSS), carbon nanotubes (CNTs), graphene and metallic nanowires (NWs). One of the attractive properties some of these materials have is their ability to be processed in the liquid phase because of the solubility properties they possess from their nanoscale forms of highly conducting wires or sheets therefore making it possible to cast these materials from solution into films, resulting in a shift away from high temperature, high vacuum, expensive processes, and towards high volume, high throughput via low cost solution coating methods for thin film electronics [5].

Hybrid Transparent conductive films based on a combination of metals with oxides or polymers have been explored by a few authors such as Iskandar *et al.* in which they reported on hybrid films composed of Graphene-carbon nanotube hybrid transparent conductive films and other reports of reduced graphene oxide and copper nanowires (NWs) [6]. Other possible material combinations to form nanocomposite electrodes such as carbon nanotube/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)(CNT/PEDOT:PSS); Carbon nanotube/Graphene, silver nanowire/metal oxide have also been explored to improve electrical and optical properties of these films [7] [8][9]. The relative ease in processing and formulating nanomaterials via solution-based methods whilst these materials retain their improved properties in terms of durability, flexibility, conductivity, transparency are going to be highly beneficial to the electronic sector because they give a pathway for device manufacture centred on an existing roll-to-roll coating equipment and infrastructure from the ink onto thin film fabrication on these devices [10]. The combination of low-cost materials, high volume and cheap roll-to-roll coating methods, superior film mechanical properties, and suitable electro-optical performance has led to continued research into these materials [11]. They are also beneficial to other sectors such as healthcare, energy storage, construction, packaging, and consumer goods because of the added characteristics that these materials possess in terms of their high strength and durability.

One of the most promising contenders amongst these materials are silver nanowire (AgNW) films because of their remarkable optical and electronic properties, their ability to be solution processed and their deposition possibilities via a scalable coating and printing technique at low temperatures. However, before implementing these silver nanowire (AgNW) films on optoelectronic devices, several concerns need to be dealt with to avoid device degradation. Silver nanowire (AgNW) networks have huge surface roughness, high junction resistance in the gaps between wire-to-wire connections in their morphology, poor adhesion to substrates, thermal instability at extremely high temperatures and limited contact area with an adjacent layer in a layered device stack [5], [13]. The achievement of maximum light transmittance and minimum sheet resistance through a layer of the film poses a dilemma because the two contrasting parameters must be well adjusted for optimum performance. The approach in solving this dilemma is centred on fabricating and electrically characterising a layer of thin film of silver nanowire electrode. The morphological, optical, and electrical characteristics of these silver nanowire contact electrodes were then investigated as a function of processing parameters for better optimization to be successfully integrated into organic field-effect transistor devices. To improve the inherent, poor uniformity in conductivity and lower the high surface roughness of silver nanowire films, composite films based on a silver nanowire network and polyvinyl alcohol for Organic Thin Film Transistor (OTFT) applications have been studied in this thesis.

1.2. Outline of the thesis

This thesis discusses the successful fabrication and characterisation of High and low voltage organic field effect transistors using high-capacitance gate dielectrics. Following this introductory chapter, relevant literature concerning operating principles of organic field-effect transistors, their device physics, device operation and a review of transparent conducting materials is evaluated in chapter 2. Methodology and experimental work are thoroughly described in chapter 3, a large section of which is allocated to nanocomposite preparation and then progressing into device structure and fabrication. Chapter 4 comprises of results and discussions from the fabrication of High and Low Voltage Organic Field-Effect Transistors. Finally, conclusions are presented in chapter 5 alongside discussions on potential future work in chapter 6.

Chapter 2

2. Literature Review

2.1.1. Thin Film transistor

Thin-film transistor (TFT) is a unique type of field-effect transistor (FET) whose practical components are thin-film materials including the active semiconductor, dielectric, and electrode layers.

Thin-film transistors are fabricated by depositing the thin films of an active semiconductor, a dielectric layer and Source (S) and Drain (D) contacts as well as Gate electrode contacts on a glass substrate as shown in figure 2.1.1.

Glass is chosen since it is nonconductive with exceptional optical transparency; it is also nonreactive to the chemicals used in semiconductor processing. In contrast, in the assembly of a typical transistor, the substrate used is a semiconductor material, typically a silicon wafer.

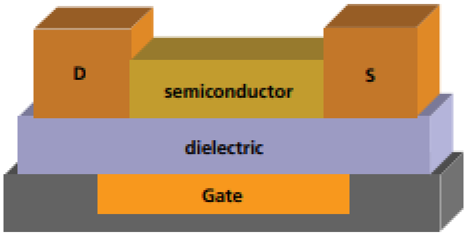


Figure 2.1.1. Schematic Structure of a Thin Film Transistor (TFT). [27]

The Thin Film Transistor (Field Effect Transistor) was created by Julius Edgar Lilienfeld in 1925 and first patented in 1934 by Oskar Heil, but regrettably, it was not realistically used at that time because the manufacture of high-quality thin films was still decades away.

In the 1940s and 1950s, functional semiconducting devices based on the crystalline bulk semiconductors [such as junction field-effect transistors (JFET), bipolar junction transistors (BJT), and metal-oxide-semiconductor field-effect transistors (MOSFET)] were successively created, producing a great effect on logic circuit and digital electronic advancement. Until 1962, Weimer in the RCA laboratory reported the first practical Thin Film Transistor (TFT).

The year 1964 proclaimed the introduction of metal-oxide-semiconductor thin film transistor by Klasens and Koelmans [39]. They displayed a Thin Film Transistor on a glass substrate, consisting of aluminium (Al) gate electrode, anodized aluminium oxide (Al_2O_3) gate dielectric, evaporated tin dioxide (SnO_2) semiconductor, and Source/Drain contacts.

Afterwards, other authors exhibited the likelihood of transistor realization on various semiconductor thin films such as Cadmium selenide (CdSe), Tellurium (Te), Cadmium Telluride (CdTe), Zinc Telluride (ZnTe), Indium antimonide (InSb), Zinc Oxide: Lithium (ZnO: Li), and Lead sulfide (PbS). In the meantime, hydrogenated amorphous Silicon thin-film technology was well created and the first hydrogenated amorphous Silicon thin film transistor was developed by LeComber et al. [36] in 1979.

Bearing in mind the more appealing industry potentials of Silicon-based method, many researchers put their works on the manufacture of Hydrogenated Amorphous Silicon thin film transistor -Liquid Crystal Displays.

Irrespective of which semiconductor is selected for Thin Film Transistors, there is one metric that is often deemed to be the most important: the charge carrier mobility (μ). The mobility characterizes how quickly charge carriers can move through a given semiconductor.

Even though Hydrogenated Amorphous Silicon thin film transistors possess a low field-effect mobility ($\mu < 1cm^2/V.\ s$) that constrains the ultimate speed of devices, the silicon-based Thin Film Transistors moved into the industry immediately because of their high field effect mobility, and successfully dominated the large area Liquid Crystal Display product market since the mid-1980s.

Furthermore, public concern in high-performance or more environmentally friendly electronics urged the utilisation of other advanced material-based electronics. In 1986, Koezuka et al. [37] reported the first Field Effect Transistor (FET) based on the organic semiconductor thin film, and in 1990, Tsumura et al. [37] displayed an all-organic “soft” Thin Film Transistor with the field-effect mobility (μ) like that of Hydrogenated Amorphous Silicon thin film transistors. Subsequently, organic Thin Film Transistors showed a remarkable development in research with regards to properties, processability, cost, and compatibility with lightweight, flexible plastic displays.

Since the commencement of the 21st century, with the advancement of many thin-film deposition methods, Thin Film Transistors with high-performance or other distinctive characteristics were constantly utilized, mostly comprising of metal oxide, and organic Thin Film Transistors.

In 2003, various reports demonstrated a high μ larger than $1\ cm^2/V.\ s$ for metal oxide Thin Film Transistors such as Zinc Oxide (ZnO) thin film transistors, comparable to and even surpassing that of Hydrogenated Amorphous Silicon or organic thin film transistors. Simultaneously, other binary metal-oxide-semiconductors like Indium oxide (In_2O_3) and Tin dioxide (SnO_2) were also utilized as the channel layers, likewise yielding good performance.

The Field effect mobility (μ) values of organic Thin Film Transistors have increased dramatically and now surpass those of thin-film amorphous silicon devices. Also, organic Thin Film Transistors possess remarkable benefits such as low processing temperature, low cost, and excellent flexibility, demonstrating their possible applications in flexible and/or printed electronics. Though, diverse organic active materials have distracted researchers, organic Thin Film

Transistors have other severe stability problems than inorganic ones, constraining their real application [33].

Today, and after several decades of research and development, the amorphous silicon Thin Film Transistors remains the main technology utilized to drive liquid crystal displays (LCDs). Yet, as new display technologies are being developed, the centre of Thin Film Transistors research is moving to new organic semiconductor materials—a move encouraged on by the limitations of the established technologies, or the useful characteristics proposed by new categories of materials, like metal oxides and organic semiconductors. Thin Film Transistor (TFT)- measured mobility is recognized to depend on several extrinsic factors. This has been bad news for carbon-based organic semiconductors, which, for a long period, possessed mobility values that were a world away from their inorganic counterparts.

Nonetheless, the same distinctive chemical nature that is accountable for their low mobilities also gives organic semiconductors tremendous processing versatility, as well as exceptional mechanical properties, such as flexibility and stretchability. The latter qualities gave birth to the idea of a foldable, flexible electronics market that caught the imagination of people all over the world. This interest for flexible, printed electronics has driven vast research efforts to improve the critically low mobilities of organic semiconductors, measured in organic Thin Film Transistors (OTFTs) [34].

Nonetheless, with the latest increase on field-effect mobility of Thin Film Transistors fabricated with the active layer deposited from solution processes, more consideration has been attracted to the likelihood of utilizing remarkably simple and low-cost deposition techniques to achieve high-performance Thin Film Transistors. Solution-based deposition processes permit the use of methods like dip coating, spin coating, spray coating, ink-jet printing, silk screen and many others which are well suited to large-area, flexible, affordable, and scalable applications.

Spin coating is a widespread utilized deposition method which produces very thin (ranging from few nanometres up to micrometres) and uniform films by spreading a solution of the chosen material onto cleaned substrates and making them spin at high rotation speeds (about 1000–

8000 rpm) promoting solvent evaporation. The method is highly effective in the formation of organic or polymeric films but can be used to deposit inorganic materials solutions or suspensions as well [35].

Thin film transistor (TFT) is thought to be one of the most appropriate devices to fabricate high performance flexible display due to their advantages in high carrier mobility, good uniformity, low cost, and low process temperature. Thin Film Transistors has attracted much awareness of the scientists and industrial circles. The high-performance electrode is the main technology to realize the low power consumption, ultra-high resolution, and high reliability application in flexible display.

Thin Film Transistor is different from metal oxide semiconductor field-effect transistor (MOSFET) in some ways. Primarily, Thin Film Transistor works in accumulation layer while metal oxide semiconductor field-effect transistor (MOSFET) works under inversion layer. Secondly, Thin Film Transistor (TFT) is amorphous in nature as compared to metal oxide semiconductor field-effect transistor (MOSFET), which is crystalline in nature. Thirdly, Thin Film Transistor is undoped while metal oxide semiconductor field-effect transistor (MOSFET) is mostly Silicon-doped.

For the working of a thin film transistor (TFT), the applied gate voltage (V_G) regulates the electron flow from source to drain. For positive gate voltage, electrons are attracted towards the bottom side of the semiconductor layer and conduct a channel. Then, the voltage applied between the two terminals result in current flow.

Thin Film Transistors can be operated in depletion mode or enhancement mode reliant on whether it requires a gate voltage to induce the conduction in the channel. When no gate voltage is applied, the channel conductance is low for enhanced mode of operation. Consequently, a low carrier density in the channel is essential to achieve this mode. A channel must be induced in case of enhancement mode. In this mode, channel enhances on increasing the gate source voltage. Then applying voltage between the drain and source terminals causes the drain current to flow. While in case of depletion mode, if we apply the drain source voltage, the drain current will flow for zero gate source voltage [78].

2.1.2. Organic Electronic Materials

Organic electronics, plastic electronics, or polymer electronics is a branch of materials science dealing with electrically conductive polymers and conductive small molecules. It is called ‘organic’ electronics because the polymers and small molecules are carbon based. This contrasts with traditional electronics, which depend on inorganic conductors and semiconductors, such as copper and silicon, respectively. Today, electronics researchers are more driven on decreasing the size of semiconductor devices to their fundamental limits and this has headed to the innovation of conductive organic electronic materials such as conductive polymers and small molecules.

The discovery of the electrical conduction in organic materials can be traced to the year 1862 when Henry Letheby acquired a partly conductive material by anodic oxidation of aniline in sulfuric acid [26]. Heeger, MacDiarmid, and Shirakawa found out in the 1970s that the polymer polyacetylene, after certain adjustments, can be made conductive [76] [77]. Doped polyacetylene can be used to form a new group of conducting polymers and the electrical conductivity of the material can be methodically tuned over a range of 11 orders of magnitude. In 2000, the Nobel prize in Chemistry was given to Heeger, MacDiarmid, and Shirakawa for their findings.

At the end of the 1980s, a new category of conductive organic materials was established. Many research groups displayed organic devices using a small molecule, or can be called oligomer, rather than a polymer. Contrary to polymeric materials, small molecules are rather insoluble in solvents. Therefore, deposition techniques based on vacuum sublimation were introduced for depositing thin films of a semiconducting small molecule. Peng et al. [17] fabricated α-sexithiophene (α-6T)-based Organic Thin Film Transistors with different kinds of organic polymer insulators. With the assistance of polymer dielectrics, including polyvinyl alcohol (PVA) and cyanoethyl pullulan (CYEPL), the electrical performance of the Organic Thin Film Transistors has been improved compared with that on Silicon dioxide (SiO_2) layer.

In solid-state physics, the electron mobility describes how rapidly an electron can move through a metal or semiconductor, and the dielectric constant is a measure of the amount of electric potential energy, in the form of induced polarization that is stored in a given volume of material under the action of an electric field. A strong relationship was discovered between the dielectric constant of the dielectric layer and the mobility. In 1992, Horowitz et al. [19] reported Organic Thin Film Transistors made with various π-conjugated oligomers, including oligothiophene series and polyacenes. Also, several inorganic and organic insulators were used in the study. The mobility was shown to increase as the conjugation length of the oligomer increased. They also found that the charge transport of the device is primarily controlled by the interface between the semiconductor and the dielectric, which is pioneer research in this field.

In 1994, Garnier et al. [20] developed Organic Thin Film Transistors from semiconducting polymers by printing methodologies. The performances of the devices are unresponsive to mechanical treatments, such as bending or twisting. Their reported technology unlocked the way for low-cost and large-area flexible electronics. Later, Bao et al. [21] reported the printed organic transistor where in all the major components can be easily screen-printed. This transistor had a polyimide dielectric layer, a regioregular poly(3-alkythiophene) (P3AT) semiconducting layer, and two silver electrodes.

High-*k* dielectric materials began to be used in Organic Thin Film Transistors by researchers from 1999. Dimitrakopoulos et al. [22], [23] from IBM research group first deduced the gate voltage dependence of the mobility in pentacene-based transistors and this result is based on the interaction of charge carriers with localized trap levels in the band gap. They demonstrated high-performance low-voltage organic transistors on transparent plastic substrates in the report.

Tate et al. [24] showed the joint use of two techniques for developing organic transistors that can operate at low voltages: anodization for thin (similar to 50 nm), high-capacitance gate dielectrics and microcontact printing on electroless silver for high-resolution (similar to 1 micrometre (1μm) source/drain electrodes. The near room temperature methods are appealing and compatible with organic semiconductors and flexible substrates, also they are suitable for roll-to-roll printing technology. In the same year, Sirringhaus et al. [25] showed direct inkjet printing of complete transistor circuits [26].

Conductive polymers are lighter, more flexible, and less expensive than inorganic conductors. This makes them a wanted replacement in many applications. It also generates the likelihood of new applications that would be impossible using copper or silicon. Organic electronics not only includes organic semiconductors, but also organic dielectrics and conductors.

Generally, organic conductive polymers have a higher resistance and therefore conduct electricity poorly and inefficiently, as compared to inorganic conductors. Researchers presently are discovering ways of “doping” organic semiconductors, like melanin, with relatively small quantities of conductive metals to enhance conductivity [28].

The primary element in organic electronics is the semiconducting, conjugated organic materials, which can be processed into devices from solution, allowing large area and low-cost fabrication. Also, many organic semiconductors are mechanically flexible and therefore applicable to bendable electronic elements [29].

The fabrication temperatures of organic devices are typically much lower than those of inorganic devices due to their weakly binding van der Waals forces [10]. Hence, they can be developed via high-throughput low-temperature methods that allow one of the various well-established printing techniques. Besides, although the intrinsic van der Waals forces of organic materials give them their flexibility, it also means these materials have a low melting point and glass transition temperature (Tg).

A typical glass transition temperature (Tg) in “practical” materials can be lower than 100 degrees centigrade; therefore, thin films prepared by organic materials are not thermally stable. As the temperature of the film reaches its glass transition temperature (Tg), the organic film tends to crystallize and delaminate from its adjacent contact electrode.

Organic semiconductors have caught the interest of the electronics industry for good reasons. A widespread range of properties, such as solubility in organic solvents and they can be finely tuned via chemical synthesis. The tunability facilitates the engineering of molecules to fit specific requirements.

Another appealing feature involves processing. Polymer coatings can be effortlessly applied over large areas and to a variety of substrates, including mechanically flexible ones. Related with the ease of processing is the potential for low-cost fabrication. Arrays of pixelated organic Light Emitting Diodes have been broadly created for application in high-performance displays, and large-area displays are now close to large-scale manufacturing.

Although, low charge mobility compared to single crystalline silicon, and other identifying features, constrain the variety of applications foreseen for organics. Organic electronics is not meant to replace traditional silicon electronics, but rather to complement it and extend its capabilities [30].

As mentioned in the past, there are two major classes in the organic semiconductor family: small molecular weight materials and polymers. A resolution to the request of a cheap, probably slower, and large area compatible electronics was the discovery of organic conjugated molecules – short and small molecular weight oligomers, as well as long and high molecular weight polymers.

They both have the common property of a conjugated π-electron system that is formed by the p_z-orbital of sp_2-hybridized carbon atom as shown in Figure 2.1.2. The significant difference between these two classes of materials lies in the formation of thin films. The small molecular weight materials are typically deposited from the gas phase by sublimation or evaporation; while polymers form the film from solution processing for example spin-coating, dip-coating [31].

Carbon-based molecular semiconductors share a common structural feature: The bonding in the molecule or along the polymer backbone consists of alternating single and double carbon–carbon bonds. This alternation is termed conjugation.

Double bonds form when the carbon atoms bond through sp^2 hybrid orbitals, which produces sigma (σ) bonds within a plane and leaves the out-of-plane p_z orbitals nonhybridized. Overlap of p_z orbitals on adjacent carbons can form π orbitals, which are significantly delocalized over the molecule or along segments of the polymer chain.

The overlap of hybrid sp orbitals gives rise to σ and σ* bonds, while the p_z orbitals can overlap keeping their axes parallel to each other and form π and π* bonds as shown in figure 2.1.2. The filled π bonding orbitals form the valence states, and the empty π* antibonding orbitals form the conduction states. In organic materials, the highest energy level of π bonding in energy levels is called highest occupied molecular orbital (HOMO) and the lowest energy level of π* bonding is called lowest unoccupied molecular orbital (LUMO).

The highest occupied molecular orbital (HOMO) corresponds to the valence band in the inorganic semiconductor materials, and the lowest unoccupied molecular orbital (LUMO) can be considered as a conduction band in the inorganic semiconductor materials [30]. In summary, organic semiconductors based on polymers or small molecules consist of π-conjugated bonds, which lead to delocalized filled and empty π-orbitals that affect the electrical and optical behavior of the material.

In comparison to organics, in the solid state, the molecules weakly interact by π-stacking, van der Waals and dipole–dipole forces, which are responsible for the material’s properties [29].

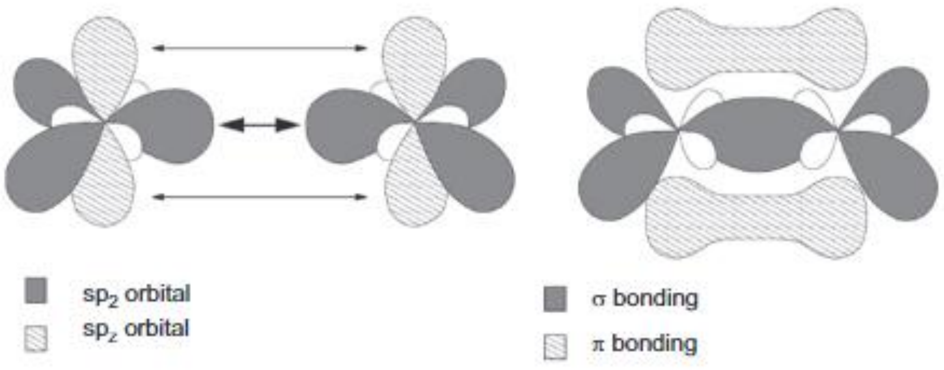


Figure 2.1.2. Left: Orbitals sp_2 and sp_z. Right: sigma and pi bonding in the simplest conjugated pi-electron system. [31]

As soft materials with only van der Waals intermolecular interactions, molecular and polymeric materials must be processed in ways that differ considerably from crystalline semiconductors like silicon. Certainly, a great deal of the interest in organics has been concentrated on finding new ways to form useful structures for devices. Processing from the liquid phase is specifically attractive, because the technique is scalable to large areas and can also permit direct patterning on a substrate.

But solution processing is of constrained use for making molecular semiconductors since they usually have limited solubility and they do not form continuous thin films, tending instead to crystallize. While for polymers, solution processing is appealing for many reasons. It is convenient, can form thin high-quality films, and can permit molecular-scale organization of one material on another. The primary difficulty lies in understanding and controlling the growth of these materials to achieve films with well-defined structure and morphology—and in understanding the molecular origins of charge traps and other defects that molecular semiconductors contain [30].

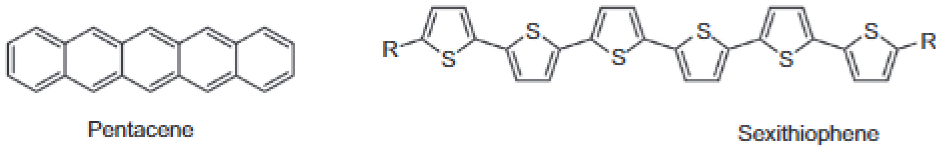


Figure 2.1.2.1. Chemical structure of two popular small molecular organic semiconductors, namely, pentacene and sexithiophene, respectively. [31]

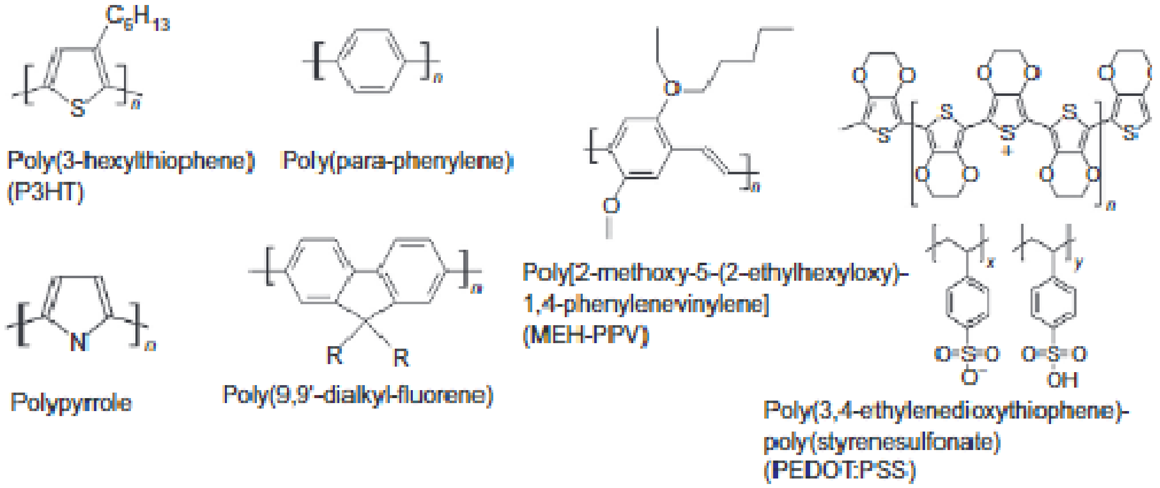


Figure 2.1.2.2. Chemical structure of some conjugated semiconducting polymers. [31]

There are two types of organic semiconductors based on the type of majority charge carriers: p-type (holes as major charge carriers) and n-type (electrons as major charge carriers). A material that transports positive charge is known as a p-type and a material that transports negative charge is known as n-type. To assist charge transport, the organic semiconductor layer usually consists of π conjugated oligomers or polymers, in which the π – π stacking direction should preferably be along the direction of current flow. This compels the semiconductor molecules to self-assemble into a certain orientation upon either vapor or solution deposition.

2.1.3. Geometry and operating principles of organic field-effect transistors (OFETs)

There is a huge enthusiasm in both academia and industry regarding the study of organic field-effect transistors (OFETs), organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and sensors.

An important parameter in device operation is the field-effect mobility (μ) of the charge carriers within the semiconductor layer. For example, in Organic Field Effect Transistors, μ is the figure of merit for device quality, with a high mobility being most wanted to improve the operational speed. Mobility is an intricate property, because it is reliant on both the molecular structure of the organic semiconductor and its microstructure, but also the quality of the contacts, interfaces, and other factors of intrinsic or extrinsic nature.

The maximum stated mobilities for organic semiconductors have improved five orders of magnitude for the last 25 years because of increased know-how on the issues that regulate the transport in organic materials and devices. Regardless of this remarkable growth, the mobility is still modest (1–10 cm^2 /V. s) and the current state-of-the art performance is still limited to low operation frequencies.

The Organic Field Effect Transistor is a three-terminal device (Fig.4), with the three contacts known as gate, drain, and source, and an organic semiconductor as the active layer. If the semiconductor is in a thin-film form, the devices are referred to as ‘organic thin-film transistors’ (OTFTs).

Despite their modest operation, they present increased technological interest because of their decreased difficulties in terms of processing capabilities. Their utilization is mainly appealing in combination with solution-based manufacturing methods. Quick deposition by the utilization of roll-to-roll processing, inkjet printing or spray deposition may permit their manufacture in large volumes and at low cost per unit area, and hence the introduction of the concept of ‘electronics everywhere. The functioning of Organic Field Effect Transistors has improved greatly since the first reports, which date from the 1980s, and field-effect mobilities matching hydrogenated amorphous silicon – near 1 cm^2 /V. s – were reported in vacuum sublimed and solution deposited Organic Field Effect Transistors.

In Organic Field Effect Transistors operation, a channel forms at the organic semiconductor/gate insulator interface and the electric field applied at the gate electrode regulates the density of the charge carriers accumulated at the interface. The current between source and drain (I_D) is modulated by the gate-source voltage (V_{GS}) and the drain-source voltage (V_{DS}). This presents a huge control over the electrical conductivity of the channel by tuning the density of charge carriers over a wide range [41].

The distance between source and drain electrodes is known as channel length (L). The width of source and drain electrodes is known as channel width (W). In the case of an Organic Field Effect Transistor, the gate electrode can be a metal or a conducting polymer. For the gate dielectrics, inorganic insulators, such as Silicon dioxide (SiO_2), or polymeric insulators, such as poly (methyl methacrylate) (PMMA) or poly(4-vinylphenol) (PVP), are usually utilized according to the transistor structure. The source and drain electrodes, which inject charges into the semiconductor, are typically high work function metals for example gold, but conducting polymers (For example, poly (3, 4-ethylenedioxythiophene) poly (styrene sulfonate (PEDOT: PSS), Polyaniline (PANI), which can be printed, are utilized also [31].

Many device architectures can be fabricated that are reliant on the order in which the layers are deposited, as shown in Figure 2.1.3. Bottom contact, bottom gate structures (Fig.4a) are usually selected for rapid screening of newly synthesized organic semiconductor compounds or testing new deposition techniques because of their easy fabrication and the least processing required on the easily degradable organic layers. In this architecture, substrates consisting of gate electrode/gate dielectric/source and drain contacts are prefabricated and the organic semiconductor is deposited during the last stage of the fabrication process. Gold or silver are typically used as contact materials because of their high electrical conductivity, and Silicon dioxide (SiO_2), Aluminium oxide (Al_2O_3) or other inorganic oxides or nitrides as gate dielectrics.

Their disadvantage is the high operating voltages (>20 V) that they need because of the thickness required to minimize the leakage currents. Substituting these dielectrics with molecular self-assembled monolayers (SAMs) permits establishment of high-mobility Organic Field Effect Transistors that function with supply voltages lower than 2 Volts. With the utilization of Self Assembled Monolayers, chemists can gain better control of the self-assembly of organic electronic molecules and turn them into ordered patterns. Improved controlled self-assembly needs a better understanding of the electronic properties of organic materials, especially when those materials are in contact with other materials (i.e., their interfacial behavior) to improve mobility values.

The selection of dielectrics is essential not only in influencing the operating voltages, but also in regulating the field effect mobility of the Organic Field Effect Transistors by the polarization effects that they may introduce at the interface with the organic semiconductors.

Due to the increase in the dielectric constant of the gate dielectric material, there is also an increase in the dielectric polarizability, resulting in formation of Fröhlich polarons [41]. This polaronic coupling causes scattering events in the transistor channel, thus reducing mobility. Theoretical calculations and many experimental reports forecast that those structures in Figure. 2.1.3b and c may permit superior device performance because of less serious contact effects. Truly, measurements performed on Organic Field Effect Transistors structures consistent with Figure. 2.1.3b, with Cytop gate dielectric, showed low hysteresis and mobilities as high as 2.4 cm^2 / V.s.

Manufacture of Field Effect Transistors with top contacts gives manufacturing challenges related to the degradation of the organic semiconductors upon their exposure to high-energy metal atoms when techniques such as e-beam or thermal evaporation are utilized. However, many reports demonstrate good electrical properties in device structures as shown in Fig. 2.1.3c. A newly established soft contact deposition technique known as ‘flip-chip lamination’ may permit for additional growth in fabrication of top-contact Organic Field Effect Transistors. Mobilities as high as 8cm^2/V.s were shown in transistor architectures such as Fig.2.1.3d in which they were fabricated on rubrene single crystals with parylene top-gate insulator. Top-gate Thin Film Transistors (Fig. 2.1.3b and d) also offer encapsulation of organic layer by the gate dielectric and gate electrode, therefore enhancing environmental stability [41].

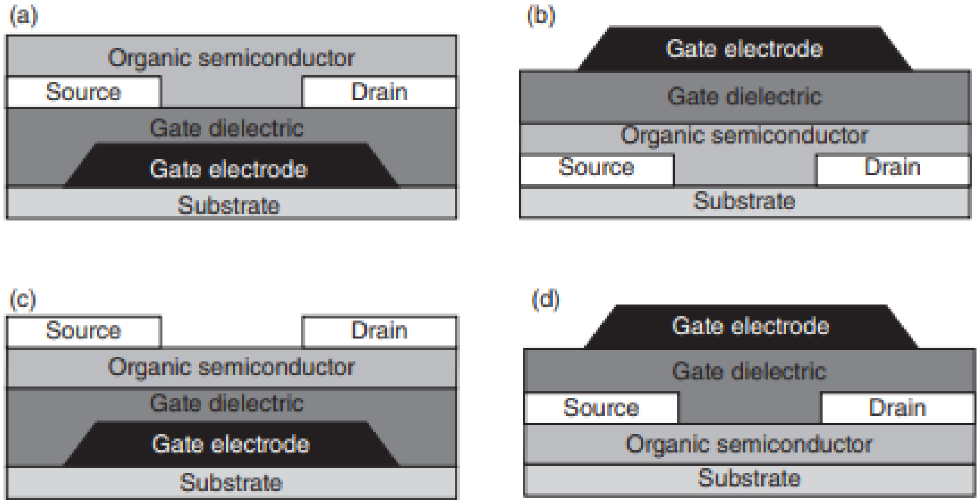


Figure 2.1.3. Cross-section of the most common FET structures. Each layer is represented in a different shade. (a) Bottom-gate, bottom contacts FET. (b) Top- gate, bottom contacts FET. (c) Bottom-gate, top contacts FET. (d) Top-gate, top contacts FET. [41]

The operation of an Organic Field Effect Transistor is considerably distinctive from that of a silicon metal oxide semiconductor field-effect transistor (MOSFET), which operates in inversion mode. In Silicon metal oxide semiconductor field-effect transistors (MOSFETs) the regions adjacent to the source and drain contacts are heavily doped, and as a result a flow of minority carriers is induced to form the Drain current (I_D) current. Organic Field Effect Transistors function on intrinsic semiconductors and operate in accumulation mode. At this point the channel of the transistor develops in the organic semiconductor at its interface with the gate insulator as follows: holes are accumulated when a negative V_{GS} is applied (p-type conduction), and electrons when a positive V_{GS} is applied (n-type conduction).

The type of conduction starts from the intrinsic properties of the semiconductor and from the selection of the contact material. Organic Field Effect Transistors have the electrical performance evaluated primarily by two characteristics known as current–voltage curves, that is, the output and the transfer curves. The output curve is defined by the drain-source current (I_{DS}) versus the drain-source voltage (V_{DS}) at different constant values of the gate voltage (Vg), while the transfer curve is obtained by measuring I_{DS} versus Vg at different constant values of V_{DS}.

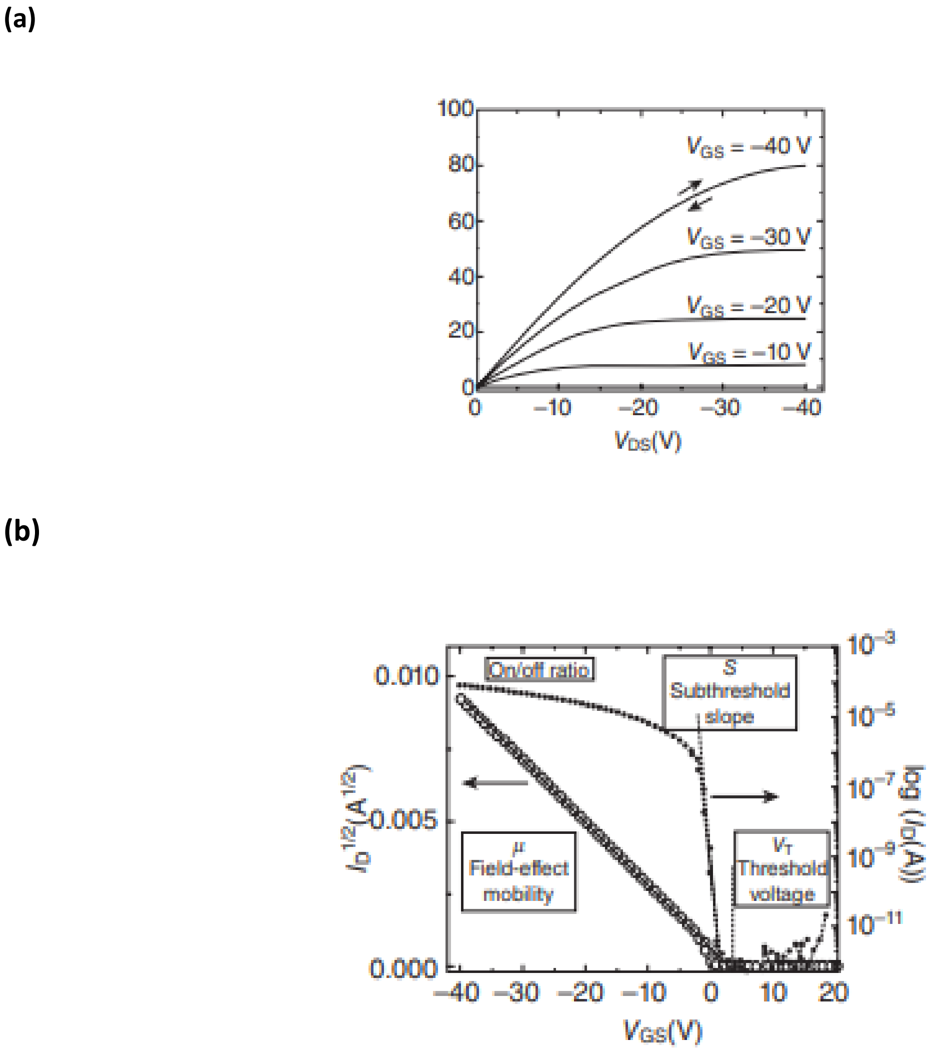


Figure 2.1.3.1. Electrical characteristics of Organic Field Effect Transistors: (a) Output curve - evolution of the drain current I_D with the drain voltage V_{DS} for various gate voltages, V_{GS}. (b) Transfer curve - evolution of the drain current I_D with the gate voltage in the saturation regime. [41]

Organic semiconductors are mainly p-type, and only a few n-type conductors have been found. Ambipolar Field Effect Transistors operate in both voltage regimes and were shown on donor-acceptor blends or alternating layers, and in a constrained number of small-band gap organic semiconductors that were able to transport both electrons and holes.

The device is active (i.e., a drain current is formed) when the gate voltage (V_g) value exceeds the value of the threshold voltage (V_T). However, yet at lower gate voltages, a small current is existing because of diffusion of charge carriers caused by their thermal energy.

The most crucial parameters in describing a Field Effect Transistor are its field-effect mobility μ, threshold voltage V_T, "on/off" ratio and inverse subthreshold slope (subthreshold swing) SS. Field-effect mobility quantifies the average charge carrier drift velocity per unit electric field and is typically reported in cm^2 /V.s ,while threshold voltage is a minimum gate voltage to induce mobile charges at the insulator/semiconductor interface (i.e. gate voltage at which the conducting channel starts to form) and is determined by the amount of traps introduced by interfacial disorder (caused, for example, by fixed charges, surface structural defects and dangling bonds) and the defects in the bulk of the semiconductor. Threshold voltage (V_T) is also often affected by the quality of source/drain contacts.

In addition to Field-effect mobility (μ) and Threshold voltage (V_T), "on/off" ratio is defined as the source-drain current ratio (I_{on}/I_{off}) between the "on" and "off" states and it is usually given as 10X while subthreshold swing (SS) is a measure of how rapidly the device switches from the "off" to the "on" state and is commonly reported in V/decade.

The 'sub-threshold regime' is quantitatively characterized by the subthreshold swing, SS. Subthreshold (SS) can be determined by taking the inverse of the slope of the log (I_D) versus V_{GS} curve – subthreshold slope (Figure 2.1.3.1b, right axis, see dashed lines for the slope) in the subthreshold regime:

$$S = \frac{\partial V_{GS}}{\partial(log I_D)} \qquad (eq. 1.1)$$

The subthreshold swing measures the speed with which the device turns on (the increase in drain current (I_D) with gate-source voltage (V_{GS}), with a low value corresponding to a device performance that is better. Values of 0.88 V/dec were approximated in pentacene Thin Film Transistors on Cytop dielectric and 0.1 V/dec with a Self-assembled monolayer (SAM) dielectric. In single crystal Field Effect Transistors typical values are 0.3–0.5 V/dec. As the subthreshold swing is regulated by the quality of the insulator/semiconductor interface, this parameter permits for estimation of the interface trap density (N_i) from Organic Field Effect Transistor data by using eq. 1.2:

$$S = \frac{kT}{e} \ln 10 \left(1 + \frac{e}{C_i} N_i\right) \qquad (eq. 1.2)$$

Here k is Boltzmann's constant, e is the elementary charge and C_i is the gate dielectric capacitance per unit area. For Silicon dioxide (SiO_2) for example, the number of traps at the organic/dielectric interface can be moderated by chemically treating this surface with Self Assembled Monolayers of organic trichlorosilane's before the deposition of the semiconductor. Consequently, a higher mobility and less hysteresis in the current – voltage (I–V) characteristics are generally achieved.

In the operation of a Field Effect Transistor, two regimes can be distinguished. In the linear regime ($V_{DS} << V_{GS} – V_T$, Figure. 2.1.3.1a), the device acts as a gate voltage controlled variable resistor: the source-drain current (I_D) increases with the applied V_{DS} voltage, following the expression in eq. 1.3:

$$I_D = \frac{W}{L} C_i \, \mu \left((V_{GS} - V_T)V_{DS} - \frac{V_{DS}^2}{2}\right) \qquad (eq. 1.3)$$

Here W and L are the channel length and width, respectively.

At higher V_{DS} ($V_{DS} >> V_{GS} - V_T$, Figure. 4b), a depletion area forms at the drain contact. Beyond this point, called 'pinch-off', the transistor operates in the saturation regime (Figure 2.1.3.1a), and I_D varies quadratically with the gate voltage (eq. 1.4):

$$I_D = \frac{W}{L}\frac{C_i}{2}\,\mu(V_{GS} - V_T)^2 \qquad (eq. 1.4)$$

It can be observed from eq. 1.3 and 1.4 that in Organic Field Effect Transistors the drain current is controlled by the applied gate-source voltage. This is quantitatively described by the transconductance gm:

$$g_m = \frac{\partial I_D}{\partial V_{GS}}|V_{DS} \qquad (eq. 1.5)$$

The transconductance is determined from the transfer characteristics of a device, at constant V_{DS} (Figure 2.1.3.1b). An increase in the drain current I_D with increased negative gate-source voltage V_{GS} is a sign for a hole-transporting organic layer. For an electron-transporting material the drain current increases when a positive gate-source voltage is applied, and for the case of ambipolar transport the current is increased for both positive and negative voltages. Figure 2.1.3.1 represents typical transfer transistor characteristics in the saturation regime of an Organic Field Effect Transistor (OFET) fabricated on an organic single crystal at the surface of octyl trichlorosilane (ODTS) treated Silicon dioxide (SiO_2) gate dielectric, with bottom Gold (Au) contacts (Figure. 4a). Following eq. 1.3 and 1.4, the field-effect mobility μ can be calculated from the slope of the I_D vs V_{GS} in the linear regime, and $(I_D)^{½}$ vs V_{GS} (curve in open circle in Figure. 2.1.3.1b) in the saturation regime respectively, using the following expressions:

$$\mu_{lin} = \frac{L}{W}\ \frac{1}{C_i V_{DS}}\frac{\partial I_D}{\partial V_{GS}} \qquad (eq. 1.6) \qquad linear\ regime$$

$$\mu_{sat} = \frac{L}{W}\frac{2}{C_i}\left(\frac{\partial\sqrt{I_D}}{\partial V_{GS}}\right)^2 \qquad (eq. 1.7) \qquad saturation\ regime$$

The intercept of this slope with the V_{GS} axis allows for determination of the threshold Voltage (V_T), with a threshold voltage near zero being required to minimize the power consumption. Increased negative or positive threshold voltage (V_T) indicates the presence of trapping or doping effects, respectively, in the transistor channel. A threshold voltage (V_T) shift may also be developed in device operation because of the interaction with the environment or bias stress effects. These effects may be of irreversible or (partially) reversible nature [41].

The on/off ratio represents the ratio between the channel currents when the transistor is in the conduction mode (I_{on}) and when it is switched off (I_{off}). Since the ideal I_{off} value is minimal (to avoid power consumption when not operating), I_{on} /I_{off} should be the highest as possible. Typical good values for on/off ratio are above 10^5–10^6 [42].

The above equations indicate that the current between the source and drain can be increased by increasing either gate -source voltage (V_{GS}) or drain–source voltage (V_{DS}). Nonetheless, these two parameters can be increased to only a certain extent. Another viable approach to minimizing gate – source (V_{GS}) and/or increasing the electrical current is adjusting the capacitance of the gate dielectric C. Whereby, C = Capacitance, ε_0 is the vacuum permittivity, K = Dielectric constant and d = thickness of the dielectric in the equation 1.8.

$$C = \frac{k\varepsilon_0}{d} \qquad (eq. 1.8)$$

The relationship (eq.1.8) makes it obvious that by either increasing the dielectric constant (k) or decreasing the thickness (d), the device current can be improved. There are requirements for gate dielectrics to be used in thin-film transistors. Apart from a high capacitance, high dielectric breakdown strength, high levels of purity, high on/off current ratios, materials processability, and device stability are also important [26].

As stated, drain current (I_D) is described in the linear and saturation regimes by Eq. (1.3) and (1.4), respectively. In the ideal case, the source-drain current should be maximum, while the gate bias voltage is as low as possible. Though, this only can be obtained when both the threshold voltage (V_T) and the subthreshold swing (SS) are satisfactorily low enabling an Organic Field Effect Transistor to be operated at a low voltage and maximum performance. Referring to Eq. (1.4), the only parameters that can be altered to compensate for the reduction in I_D are the gate dielectric capacitance (C_i) and the channel width (W) and length (L). However, W and L depend on the device geometry. Therefore, to accumulate the same number of charges within the channel of an Organic Field Effect Transistor and maintain high drain current (I_D), it is essential to increase the gate dielectric capacitance (C_i) [44].

2.1.4. Conductors

A crucial device component in organic field-effect transistors (OFETs) is the organic semiconductor/metal interface because it must ensure efficient charge injection. Usually, inorganic metals have been used in these devices using conventional lithographic fabrication methods. Metals with low or high work-functions must be chosen reliant on the type of semiconductor considered [43]. One of the vital parameters in electrode materials is the work function (ø), which is closely related to the Fermi energy (E_F) of the metal and is defined as the energy needed to move an electron to the vacuum level.

The electrode material is usually selected so that the energy level of the metal work-function aligns acceptably well with the highest occupied molecular orbital (HOMO) of the organic semiconductor for p-type conduction and the lowest unoccupied molecular orbital (LUMO) for n-type conduction. The contact material is in direct contact with the organic semiconductor, to form a Schottky contact. The energetic misalignment will result in the formation of a Schottky barrier (as shown in figure 2.1.4) hence increasing the device contact resistance. Therefore, the matching of the molecular energy levels with the metal work function is important for ensuring an efficient charge injection.

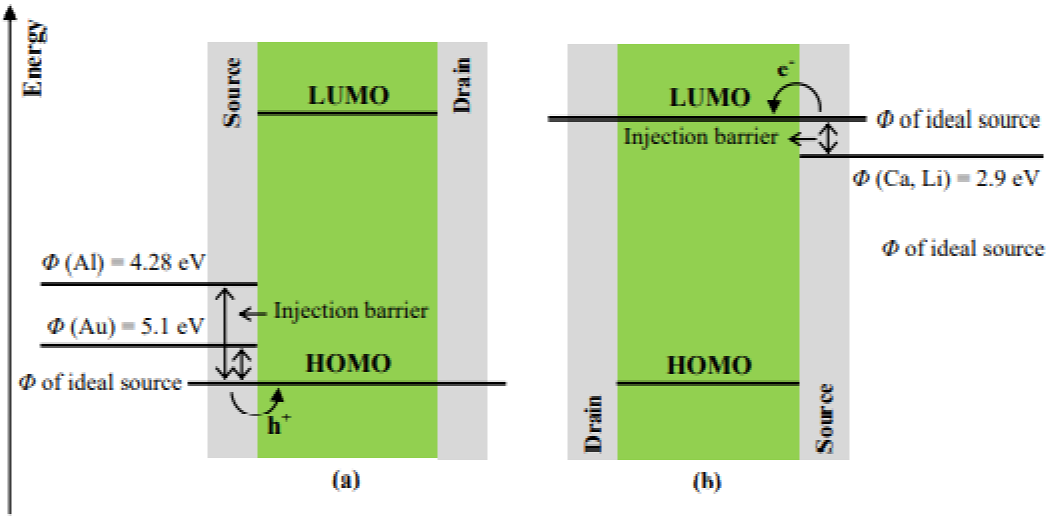


Figure 2.1.4. Energy level diagrams of (a) p-type and (b) n-type organic semiconductor and work functions of ideal and real source and drain electrodes, including injection barriers. [45]

Nevertheless, it is not always easy to select the proper material for an electrode. A relationship between the contact work-function and resulting device performance has not been created, because of the complex phenomena that happen at the metal/ organic interface. For instance, as well as the Schottky barriers and interface dipoles which develop at the semiconductor/metal interfaces, the position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels alters to some extent with molecular orientation, which in turn is highly reliant on the details of processing (surface energy, solvent, and deposition method) [41].

In certain situations, the metal has been covered with molecular self-assembled monolayers (SAM) to modify the work function, enhance the molecular order at the semiconductor/metal interface and decrease the contact resistance. Nevertheless, during the last few years, some methods have been centred on using organic metals in these Organic Field Effect Transistor devices, which have been assembled by means of both evaporation and solution-processed methods [43].

Solution processable electrode materials are required for low-cost production. Due to its requirements, a few groups have fabricated Gold (Au) or Silver (Ag) nanoparticle inks that can be cured at below 200 °C to be suited for low-cost plastic substrates [27]. Other promising electrode candidates include silver nanowires, carbon nanotube dispersion and conducting polymer solutions [27].

Higher device performances have frequently been detected, which have been credited to a variety of features, for example a more promising organic/organic interface, a better matching of energy levels or/and to a reduction of the contact resistance. Additionally, in contrast to their inorganic counterparts, organic metals permit their chemical modification and therefore the tuning of the Fermi level [43].

To obtain high device performances several distinctive device characteristics, must be considered. To be specific, the organic semiconductor/metal interface participates in a crucial role because it has a strong influence on the device contact resistance, which needs to be reduced. In an Organic Field Effect Transistor, the total resistance can be estimated by three resistances connected in series: contact resistance at the source (R_S), channel resistance (R_{CH}) and contact resistance at the drain (R_D). Preferably, ohmic source and drain contacts are wanted, which suggests that the total contact resistance ($R_C = R_S + R_D$) related to the charge injection and extraction, should be insignificant compared to the electrical resistance of the Organic Semiconductor (R_{CH}).

One of the factors that can greatly influence the contact resistance is the utilized device architecture. The source–drain contacts can be deposited below the Organic Semiconductor as in the case of Bottom Gate Bottom Contact configuration (Figure. 4a) or on the top as in the Bottom Gate Top Contact architecture (Figure. 4c). Most of the highest values of mobility for single crystal Organic Field Effect Transistors reported in the field have been obtained when bottom-contact architectures were used, whereas in the case of thin-film devices top contact geometries manage to give rise to lower contact resistances. The latter is because of the metal penetration into the Organic Semiconductor film when evaporating the top contacts thereby forming an intermixing of both components, but also due to the poor morphology of the organic thin-film semiconductors formed when bottom contact is utilized particularly at the edge of the source and drain electrodes [43]. Such an impact is also linked to a higher disorder and related higher density of traps present at the interface of the Organic Semiconductors and the electrodes that inject and extract carriers.

However, another concern in the Bottom Gate Top Contact geometry which goes in the opposite direction, is the highly resistive semiconductor area located between the contact and the conducting channel which is known to be situated in the very few Organic Semiconductor monolayers near the dielectric interface. It has been demonstrated that, in the case of thin-film Organic Field Effect Transistors, this so called ‘‘access resistance’’ has a great impact on the extracted field-effect mobility (μ) and the device performance reliant on the thickness of the active layer material [43]. Also, the evaporation at high temperature of the source and drain electrodes on the top of single crystal based Organic Field Effect Transistors is deemed to change the crystalline order at the surface of the active material and to induce defects.

But only recently, it has been demonstrated that such organic conductors may also have a huge potential in organic devices, not only as contacts but also for improving the overall device performance either by improving the Organic Field Effect Transistor mobility or the efficiency of charge injection or modifying the threshold voltage [43].

2.1.5. Insulators (high-k dielectrics)

An insulator is a material, that has a remarkably high resistivity to electric current. In other words, an absence of charge transport in insulator materials leads to insulating performance.

Dielectrics are broadly utilized in several electrical or electronic applications. The essential usage of dielectrics is an insulating material against electrical conduction. An insulator material must have a large band gap compared with the semiconductor material. Consequently, there are no states available into which the electrons from the valence band can be excited. However, there is always a breakdown voltage that will pass on adequate energy to the electrons to be excited into this band. Once this breakdown voltage is exceeded, the dielectric materials will lose the insulating properties. The other two main applications of dielectrics are capacitors and transistors, they are both crucial components of electronic logic circuits. It is well recognized that the role of the device insulator layer is as crucial as that of the semiconductor layer. In Organic Thin Film Transistors, the performance of the device is very much reliant on the physical property and chemical nature of the dielectric surface.

A capacitor is a passive electrical component comprising of a dielectric sandwiched between two electrodes as shown in Figure 2.1.5. The application of a voltage at electric fields lower than the breakdown voltage of the dielectric across this material will bring about a charge separation across the insulating layer forming the capacitor. The breakdown voltage of an insulator is the minimum voltage that causes a portion of an insulator to become electrically conductive. An ideal capacitor is characterized by a single constant parameter, the capacitance C. Higher Capacitance values show that more charge may be stored for a given voltage. Real capacitors are not complete insulators and permit a small amount of current flowing through, terming as leakage current [26].

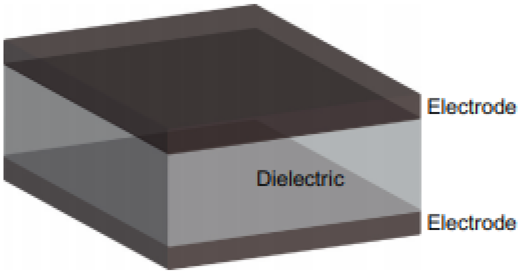


Figure 2.1.5: Schematic illustration of a parallel plate capacitor. [26]

Insulators or dielectric materials are characterized by the lack of charge transport. When an electric field I is applied, there is a shift in charge (Q) distribution in these materials. This field-induced polarization leads to dielectric behaviour and hence to capacitance C. If we imagine two electrodes separated by a distance d in a vacuum, the application of a voltage (V) between them creates an electric field that is described as E = V/d, where V = voltage applied to the capacitor and d = dielectric thickness. The charge created per unit area is proportional to this electric field, as given by eq. (1.9):

$$Q = \varepsilon_0 E = \varepsilon_0 \frac{v}{d} \qquad eq. 1.9$$

The proportionality constant between the applied voltage and the charge is known as the capacitance C, and it is shown as:

$$C = \frac{Q}{v} = \frac{\varepsilon_0}{d} \qquad eq. 1.10$$

where ε_0 is the vacuum permittivity. In a situation where a dielectric material is inserted between the electrodes, the capacitance is increased (by a factor of k, relative dielectric constant) because of the polarizability of the dielectric. In this situation, the capacitance is shown as [26]

$$C = \frac{k\varepsilon_0}{d} \qquad eq. 1.11$$

As shown in eq. (1.11), the capacitance varies directly with (k) and inversely with d (dielectric thickness). Therefore, to increase the capacitance of a parallel plate capacitor, two approaches are usually considered: the increase of C can be obtained, first, by decreasing the dielectric thickness (d) and, second, by increasing the dielectric constant (k).

Though, traditional dielectric materials such as silicon dioxide or silicon nitride, which have been utilized abundantly in various applications throughout electronic devices, have reached their basic material limits, and decreasing their thickness below 2 nanometre is particularly challenging since it results in significantly increased leakage currents, which greatly affects the transistor operation reliability and its performance. Consequently, increasing Capacitance by utilizing high dielectric constant (high-k) materials using existing or novel high-k materials emerges as a much more viable option.

Though, the development of new High dielectric materials that possess high dielectric constant (k) and at the same time show low leakage currents. Regardless of the clear benefits of these materials in capacitor and Organic Field Effect Transistor applications, they also hold severe disadvantages for example highly polar surfaces, which result in high charge trap densities mainly at the semiconductor/dielectric interface and polarization effects in the bulk, which lead to instability of the transistor threshold voltage and appearance of the source-drain current hysteresis.

In this light, various efforts to fabricate new high-k materials that can be cheaply processed using novel, low-cost deposition methods have recently been carried out. Recently, a wide range of novel high dielectric constant materials varying from high-k organic/inorganic nanocomposites, through multilayer high-k/low-k dielectric stacks to ultra-thin anodized oxides has been described as promising alternatives to the conventional high-k insulators [44].

Hence, the dielectric layer for organic transistors should be as thin as possible, and ideally with a high dielectric constant for low voltage operation [27].

Organic dielectrics applied in Organic Field Effect Transistors are usually thicker than 200 nanometres because they are usually deposited from solution by spin-coating, drop casting, or ink-jet printing, which give rise to low dielectric capacitance and consequently high operating voltage Organic Field Effect Transistors ($V_G > 20$ V). Hence, different techniques have been utilized to overcome this challenge including decreasing the gate dielectric thickness by depositing ultra-thin insulator films ($d < 10$ nanometre), utilizing high-k organic insulator materials, or doing both simultaneously. In case of utilizing high-k materials, several groups have successfully utilized high dielectric constant organic insulators and significantly lowered the operation voltage of Organic Field Effect Transistors (OFETs).

In summary, to realize low voltage operated Organic Field Effect Transistors, low values of threshold voltage and subthreshold swing are needed. Otherwise, one can obtain low voltage operated Organic Field Effect Transistors by reducing the number of traps by enhancing the dielectric/semiconductor interface. Though, both approaches are not trivial, and more materials and device research are needed to find the optimal solutions for the intended applications [44].

From the realistic point of view, high capacitance can be achieved either through the introduction of an insulator of a minimum thickness or a high-k dielectric. Though, both minimizing Dielectric Thickness (d), and maximizing dielectric constant (k), results in practical issues: a thin, fragile dielectric may lead to increased leakage currents via the insulation layer, and as a result, rise in power consumption and shorten the device life-time, while high-k insulators present unwanted effects at the organic semiconductor/insulator interface which are unfavourable morphological changes and increased level of energetic disorder in poly(crystalline) and amorphous materials, respectively generally leading to increased trapping, which results in a rise of threshold voltage V_T and inverse subthreshold slope S, as well as, lowers the field effect mobility of charge carriers in Organic Field Effect Transistors. Thus, to reserve the high performance of the organic field effect transistor’s additional coatings between the dielectric and the active layers, as well as low-k insulators have been introduced. Commonly, the insulator treatments consist of application of self-assembled monolayers (SAMs) [45].

Replacing these dielectrics with molecular self-assembled monolayers (SAMs) facilitates creation of high-mobility Organic Field Effect Transistors that operate with supply voltages lower than 2 Volts. Due to the usage of Self Assembled Monolayers (SAMs), chemists can profit from an improved control of the self-assembly of organic electronic molecules and convert them into patterns that are orderly. Enhanced controlled self-assembly requires a better knowledge of the electronic properties of organic materials, especially when those materials are in contact with other materials (i.e., their semiconductor/dielectric interfacial behaviour) to improve mobility values, threshold voltage and the Subthreshold Swing.

2.1.6. Semiconductors

There are two types of organic semiconductors based on the type of majority charge carriers: p-type (holes as major charge carriers) and n-type (electrons as major charge carriers). Organic semiconductor materials can be divided into two major classes, molecular and polymeric.

The organic semiconductors can be small molecules such as Sexithiophene, Pentacene, as shown in figure 2.1.6 and conjugated polymers such as P3HT (poly (3-hexylthiophene-2,5- diyl)) as shown in Figure 2.1.6.1 [31].

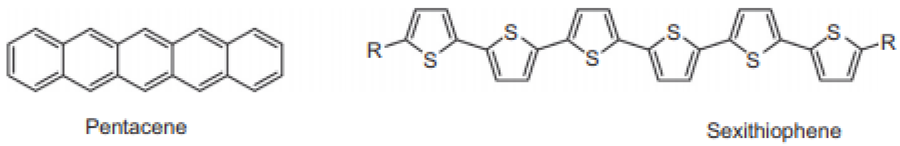


Figure 2.1.6. Chemical Structure of some popular small molecule organic semiconductors. [31]

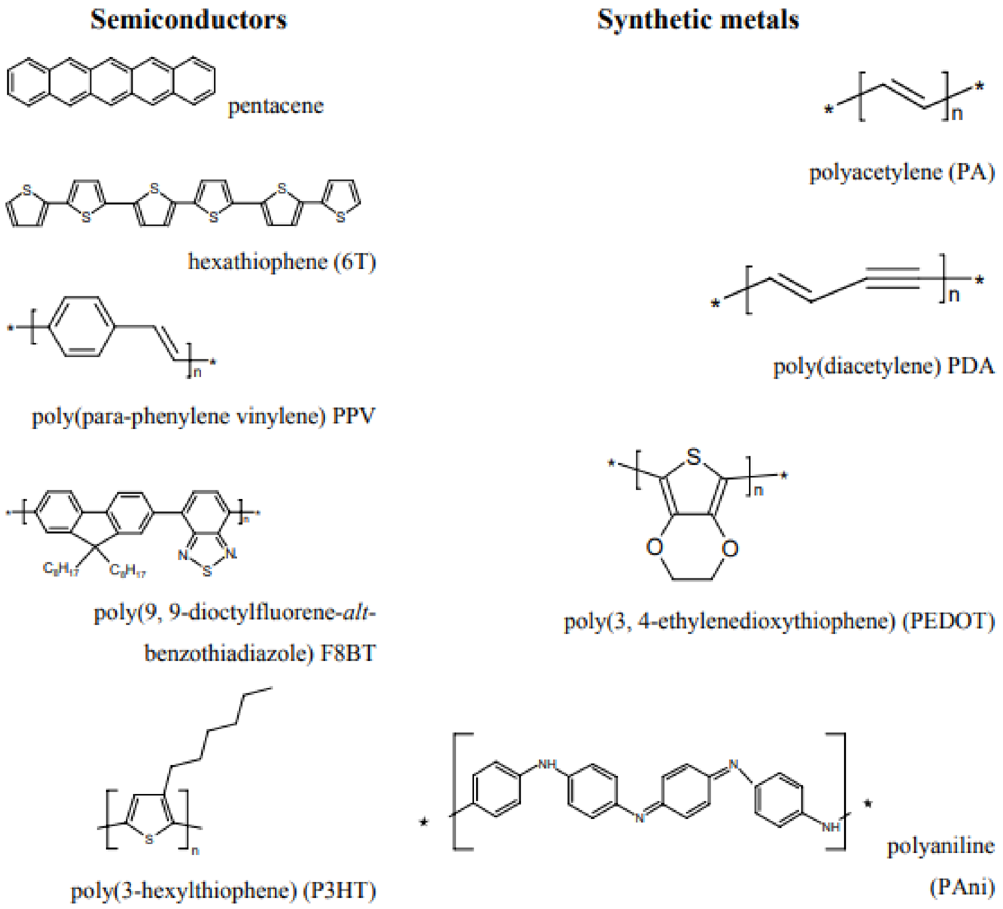


Figure 2.1.6.1. The chemical structure of some conjugated oligomers and polymers. [31]

Small molecular semiconductor materials

In the past, Tetracene and pentacene, having quite simple structures which contain benzene rings, were the most promising small organic molecules for p-channel Organic Field Effect Transistor applications. They are well known and well-researched materials concerning fabrication and characterization of Organic Field Effect Transistors. For instance, tetracene thin films can be deposited via vacuum sublimation and the achieved hole mobility is 0.15 cm^2 /V. s, whereas by using pentacene in Organic Field Effect Transistor device, which is deposited through thermal evaporation in the vacuum, the achieved hole mobility is 2.2 cm^2/V. s [46].

High-performance pentacene devices have also been developed by utilizing polymer dielectrics with carrier mobilities as great as 3 $cm^2/V.\ s$, subthreshold swings as low as 1.2 V per decade, and $I_{on}:I_{off}$ ratio of 10^5 [47].

Pentacene hole mobility is greater than the hole mobility of tetracene small molecule because pentacene has a greater molecule length than tetracene meaning that tetracene cannot deliver as great a distance for carrier movements as pentacene.

Linear thiophene oligomers and thiophene derivatives are some of other well-known organic small molecules for Organic Field Effect Transistor applications. Sexithiophene (α-6T) (Figure. 2.1.6) can be deposited by thermal evaporation method as a semiconductor in Organic Field Effect Transistors and carrier mobility of α-6T is nearly 0.1 $cm^2/V.s$. Furthermore, other thiophene-based materials such as ethyl-substituted oligothiophene have been used in Organic Field Effect Transistor applications and they demonstrate satisfactory operational performance and extraordinarily high on/off ratios. Some of the thiophene-benzene oligomers show charge carrier mobilities up to 0.42 $cm^2/V.\ s$ [46].

Polymer Semiconductor Materials

Besides, Organic Light emitting Diodes, organic thin film transistors and low cost and efficient organic solar cells are other vital applications for polymer semiconductor materials.

The usual semiconducting polymer is polythiophene. Because pure polythiophene is not soluble and hence it is challenging to form a thin film, its derivate is utilized, known as poly(3-hexylthiophene) (P3HT), which has brilliant solubility in a variety of organic solvents and they can form the thin film by several types of solution processing, such as spin-coating, dip-coating, drop-coating, screen printing, or inkjet printing.

The carrier mobility of poly(3-hexylthiophene) (P3HT) varies from 10^{-3} $cm^2/V.\ s$ to 10^{-1} $cm^2/V.\ s$ in function of the self-arrangement of molecules. In regioregular poly(3-hexylthiophene) (P3HT), crystalline lamellas in the microstructure of molecules are beneficial to the intermolecular orbital overlap and charge transfer. The formation of regioregular poly(3-hexylthiophene) (P3HT) is reliant on the degree of regioregularity, molecular weight, and deposition conditions. Also, the carrier mobility of poly(3-hexylthiophene) (P3HT) is influenced by the orientation of the regioregular lamellar, which is influenced by the substrate surface and the interconnectivity between the individual lamellar domains [31].

2.1.7. Charge carrier transport: Mobility

Charge-carrier mobility is one of the most vital figures of merit of organic semiconductors; it determines the performance of organic electronic devices such as Field Effect Transistors. Alternatively, transport properties of organic semiconductors are much more constrained than that of their inorganic counterparts. It is worth stating that even in the best organic transistors, charge transport is still regulated by the presence of chemical impurities and structural defects. The precise nature of charge transport in organic semiconductors is still not entirely clear. Though, it can be stated that a net distinction between disordered (i.e., amorphous polymers) and highly ordered semiconductors (i.e., organic single crystals) can be utilized to develop Organic Field Effect Transistors.

To develop a high-performance Organic Field Effect Transistor device, organic semiconductors must present the satisfactory circumstances related to charge injection and transport properties, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the molecules must be appropriate for electron and hole injection under applied voltage [46].

To facilitate charge transport, the organic semiconductor layer usually comprises of π-conjugated oligomers or polymers, in which the π–π stacking direction should preferably be along the current flow direction. This requires the semiconductor molecules to self-assemble into a particular orientation upon either vapor or solution deposition [27].

Charge transport in nonordered semiconductors, such as polymers, is usually defined as flying of charges by thermal activation along the distribution of localized states or shallow traps. To provide a good functioning device, the charge carrier transport mechanism happens by hopping between these localized states, causing relatively low charge carrier mobility [46].

The performance of Organic Field Effect Transistor devices is usually examined in relation to their field effect mobility as the major material parameter that determines the amount of current flowing when a gate voltage, V_g is applied. An applied electric field accelerates charged particles which are defined by the average drift velocity for the carriers involved indicating the speed of their net motion [49]. The charge carrier mobility, μ, is a measure of this proportionality between the carrier drift velocity, V_d, and the applied electric field, E: They are related by the equation:

$V_d = \mu \cdot E$ *(eq. 1.12)*

Usually, the carrier drift velocity is given in units of cm/s (or sometimes m/s) and the electric field, or electric potential per unit distance, in V/cm (resulting in the mobility being in units of $cm^2/V.\ s$). Mobility indicates how fast charge carriers flow in a certain medium as a function of applied field. The flow of carriers is the electric current thus the ability of a material to conduct electric current, I, which is measured by its electrical conductivity, σ, according to the following equation:

$I = \sigma \cdot E$ *(eq. 1.13)*

This suggests a relationship between the charge carrier mobility and the electrical conductivity.

$\sigma = n \cdot e \cdot \mu$ *(eq. 1.14)*

Where n is the number density of charge carriers and *e* is the elementary charge (the charge of single electron). The mobility is how fast individual carriers will flow whilst the conductivity is how fast net charge will flow and includes how many carriers are moving and the electrical charge of each carrier [49].

Organic semiconductor materials have their charge localized to single molecules instead of being delocalized in large bands as is the case with inorganic semiconductors. This is one of the main distinctions between organic charge transport materials and inorganic semiconductors which can be attributed to their molecular nature.

Organic semiconductors show lower mobilities than their counterpart inorganic semiconductors; though, they are still attractive because of the unique properties they offer. It is easy to modify them synthetically to suit their purpose, they can be solution processed, and are flexible [52].

2.1.8. Charge carrier transport: Traps

A trap is described as a site with an ionization potential lower than the ionization potential of the bulk material (hole trap), or with electron affinity higher than that of the bulk material (electron trap).

The weak intermolecular interactions inherent in organic semiconductors make them vulnerable to defect formation, leading to localized states in the bandgap that can trap charge carriers at different timescales [54].

Charge carrier trapping processes are inevitable in organic semiconductors, with the exclusion of exceedingly pure and defect–free single crystals. Trapping sites in organic semiconductors may have several origins; they can be made by structural defects (resulting in local positional or energetical disorder), dipoles, excimers, or guest molecules (impurities or dopants).

The most crucial parameter in the characterization of the performance of Organic Thin Film Transistors is the charge carrier mobility (µ). As introduced before, the transport in transistors happens in a very thin semiconductor layer, adjacent to the gate dielectric, in which the charge carrier density is regulated by the gate voltage. For a low charge carrier density, the charges are immobilized in traps, energetically far away from the transport states. Nevertheless, with an increasing gate voltage the traps are progressively filled, and more and more charge carriers are moved to transport states. Consequently, in a high trap density case, the charge carrier mobility would be determined from the current–voltage characteristics and would be reliant on the gate voltage.

Intriguingly, when traps are unevenly dispersed, showing a higher density at the dielectric interface, the determined mobility could decrease with an increasing charge carrier density (i.e., with increasing gate voltage. The occurrence of traps in organic semiconductors is unavoidable. The structural and morphological defects are sources of traps at the grain boundaries. Other hole or electron trap sources include: the impurities and the dopants. This greatly depends on their ionization potential and their electron affinity in relation to the host material. Regardless of the traps, there are localized states in the semiconducting layers of Organic Thin Film Transistors which are formed at the interface with the gate dielectric.

Water, oxygen, hydrated oxygen complexes or other molecules adsorbed at the dielectric surface, can create trapping states which would lead to the decrease of the drain current (I_{DS}) flowing into the transistor channel. This would influence the dependence between the evaluated charge carrier mobility and gate voltage V_G. Also, the accumulated and immobilized charge carriers at the interface are accountable for the shift of the threshold voltage V_T. Intriguingly, the charge carriers migrate gradually into the dielectric bulk when the transistor remains polarized for a long time under an applied V_G and/or V_D voltage, which induce a change of the threshold voltage (V_T) This is known as the bias–stress effect. Mathijssen et al. have showed that the trapped charges, which result in a shift in the threshold, are positioned at the dielectric gate and not in the semiconductor [55].

2.1.9. Charge injection: Ohmic contacts and contact resistance

Before a current can flow through the channel of a transistor, charges must be injected from the source electrode into the semiconductor: that means, for n-channel transistors, injection of electrons into the lowest unoccupied molecular orbital (LUMO) level and, for p-channel transistors, injection of holes into the highest occupied molecular orbital (HOMO) level of the semiconductor.

The metal-semiconductor interface is normally treated as a Mott-Schottky barrier, where the barrier height is given by the difference between the metal work function (ø) and the semiconductor highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) level.

A good ohmic contact is anticipated when the work function of the injecting metal is near the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) level of the semiconductor. Or else, a potential barrier is created, resulting in poor charge injection and non-ohmic contacts. This presents an extra resistance to the transistor (contact resistance). Contact resistance can be measured as the voltage drop at the electrodes with noncontact scanning probe potentiometry (e.g., Kelvin probe), by four-point probe measurements or by determining the resistance of transistors with different channel lengths and extrapolating to zero channel length (transfer line method).

Depending on the mobility of the semiconductor, the channel length and gate voltage contact resistance can be significant or even greater than the channel resistance and thus dominate device performance. This affects, to be specific, the linear regime of field-effect transistors since a large part of the source-drain voltage already drops at the contacts and not across the channel.

High non-ohmic contact resistance typically manifests itself in the output characteristic of a transistor as an initially suppressed and then super linear current increase in the linear region. Comparing the work function of the injecting metal with the highest occupied molecular orbital

/lowest unoccupied molecular orbital (HOMO/LUMO) levels of a semiconductor can help to determine whether charge injection is possible and whether high or low contact resistance is to be anticipated. For example, Burgi et al. [57] showed that the work function of gold (ø) 5.1 eV) is well aligned with the highest occupied molecular orbital (HOMO) level of poly(3-hexylthiophene) P3HT (4.8 eV), which leads to an extremely low contact resistance, while for copper (ø) 4.7 eV) the contact resistance was several orders of magnitude higher and almost no charge injection from aluminium (ø) 4.0 eV) was shown.

Nevertheless, the simple Mott-Schottky model is not always adequate to describe contacts. Sometimes, the interface shows an additional dipole barrier that tends to change the metal work function and therefore the interface barrier height. Deliberately presented dipoles at the metal surface, for example, through self-assembled monolayers (SAM), are beneficial to improve charge injection into organic semiconductors, as showed by de Boer et al. [58] and Hamadani et al. [59].

Furthermore, contact resistance is not just influenced by the metal and the semiconductor but as well as the device structure, for example, whether a top contact or bottom contact geometry is utilized. As stated above, the position of the injecting electrodes with respect to the gate electrode plays a role. In a staggered geometry (Bottom Contact/Top Gate and Top Contact /Bottom Gate) where the source and drain electrode overlap with the gate electrode, charges are injected over a larger area than in a coplanar (Bottom Contact/Bottom Gate) geometry. This current crowding results in a lower contact resistance for the same material organization.

Also, while bottom contacts can be reformed to change their work function, evaporated metals may present surface states in the semiconductor that assist or hamper charge injection [52].

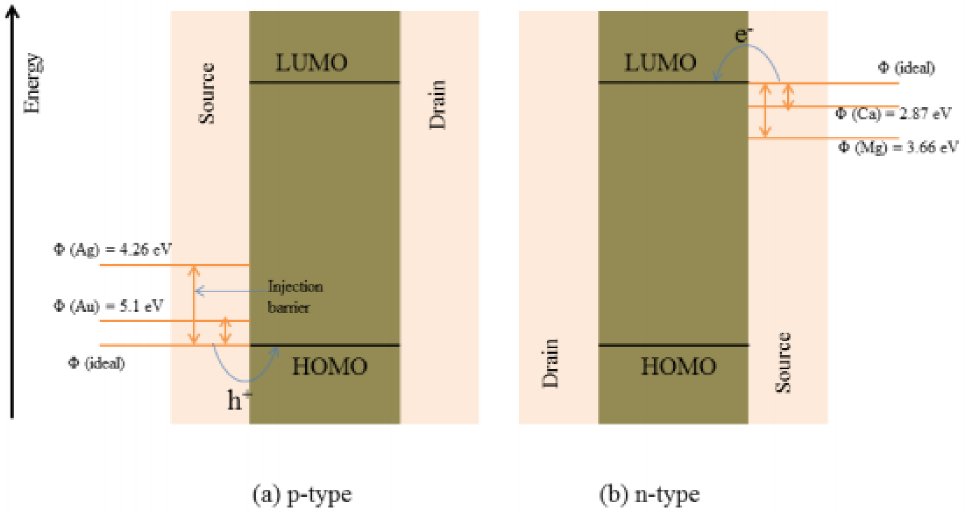


Figure 2.1.7. Energy level diagrams of an organic semiconductor with work functions of metal contacts. [45]

2.2. Transparent and conducting materials

Transparent conductive electrodes (TCE) are materials that have high electrical conductivity and high optical transmittance. These materials are an important component in optoelectronic devices and have been utilized in electronic devices such as solar cells, light-emitting diodes (LEDs), liquid crystal displays (LCDs), and touch screens [60].

The most important performance metrics for Transparent Conductive Films (TCF) are visible light transmittance (T) at 550 nm wavelength and Sheet Resistance (R_s). Low Sheet Resistance (R_s) with a high value of light Transmittance (T) are vital for optimum performance in the previously mentioned electronic devices.

To assess the quality of a Transparent Conductive Film (TCF), a figure of merit (FoM) is used to compare the electrical and optical performance of Transparent Conductive Films. The sheet resistance (R_s) and visible light transmittance (T) of a Transparent Conductive Film are connected by the equation below [61].

$$\left[T\,(\lambda) = \; 1 + \frac{188.5}{R_s} \quad \frac{\sigma_{OP}\ (\lambda)}{\sigma_{DC}}\right]^{-2} \qquad (eq. 1.15.)$$

The Figure of Merits is given as the ratio of direct current (DC) electrical conductivity and optical conductivity (σ_{DC} /σ_{OP}). Better electrical and optical performance of a Transparent Conductive Film will show a larger value of the figure of merits. Typically, a R_s lower than 1000 Ω /sq and a T greater than 85% are needed [62].

The flexibility of the Transparent Conductive Film (TCF) is another parameter that is crucial for Transparent Conductive Films because of their characteristic advantage over Indium Tin Oxide. The flexibility of a Transparent Conductive Film (TCF) can be tested by bending it repeatedly or by uniaxial tensile strain after processing. The smaller change in resistance and the greater the number of times they can be bent with a larger angle means a better flexibility. Uniformity, roughness of the surface of the film, work function, and adhesion to the substrate are other important parameters that are needed for practical application. In addition to these parameters, other factors such as Haze, light scattering effects need to be monitored depending on the electronic application requirements [63].

The highest figure of metric (FOM), up to 415 is currently possessed by metallic nanomaterials such as silver nanowires. Their performance makes them the only alternative to compete with or even exceed Indium Tin Oxide in terms of Sheet Resistance (R_s) and visible light transmittance (T).

Other materials such as Graphene and Carbon Nano Tubes (CNT) have lower Figure of Metric with an order of 1-10 for solution processed graphene and a Figure of Metric of 116 for Carbon Nano Tubes. The value of the Figure of Metric can be elevated by improving several factors which affect their performance, some of these factors include the purity of the material, level of doping, density, and the geometry of the material, although there is a challenge in enhancing these factors [62].

Metals are usually opaque, they are understood to have an insignificant bandgap between valence and conduction levels since their Fermi level is surrounded by available electron states, so any excited electron can easily transition into higher energy states and move between atoms in a crystal lattice hence when a photon of light enters a metal, they are easily absorbed by an electron instead of passing through uninterrupted but in the case of Indium Tin Oxide (ITO) they are wide band gap n type semiconductors that have a bandgap that is larger than the energy of visible light, so electrons cannot absorb photons therefore Indium Tin Oxide is transparent.

Conduction is done in Indium Tin Oxide by loosely bound electrons from oxygen atoms creating vacancies which are filled by the nearby electrons in the indium lattice [64]. Typical values of Sheet resistance (R_s)and Transmittance (T) values on glass substrate are T > 80% for a given Sheet resistance (R_s) range of 10 -100 Ω/square depending on the thickness used [65].

Indium Tin Oxide has been used in many electronic devices such as solar cells and Organic Light Emitting Diodes but as mentioned earlier, they need replacement because of their disadvantages [8]. Some work has been carried out on using other materials such as Carbon Nanotubes (CNTs) networks and Graphene which have been utilized as a front transparent contact electrode, but they have displayed inferior performance with stable flexibility.

Copper and silver nanowires have demonstrated more promising results since only a small amount might be needed to cover a certain surface to attain high Sheet Resistance (R_s) and Transmittance (T) values with bending and stretching ability and due to their network morphology, their structures can be manipulated for higher performance [8].

Other methods include the fabrication of Transparent Conductive Electrode thin films using hybrid composite materials such as silver nanowires with metal oxides, a mixture of Gold (Au) and Silver (Ag) nanowires, and silver nanowires (AgNWs) with polymer have demonstrated promising results. Thus, silver nanowire (AgNW) networks have been predicted to replace Indium Tin Oxide effectively in organic solar cells, touch screens, Organic Light Emitting Diodes (OLEDs) [12].

Few reports have also been done on solution-processed silver nanowire (AgNW) composite electrodes with either Zinc Oxide or Aluminium-doped ZnO (AZO) nanoparticles; but their performance was limited from a relatively low transparency (transmittance of 76–81% at wavelength of 550 nm) and the electrical properties of composite film were not assessed [8].

2.2.1. Conductive polymers

In the period of the 1980s, a huge range of polymers which include polypyrrole, polyaniline (PANI), polythiophene achieved widespread attention since they demonstrated substantial conductivity via the mechanism of chemical doping. Polyaniline (PANI) and polythiophene materials such as poly (3, 4-ethylenedioxythiophene) (PEDOT) stabilized by aqueous polystyrene sulfonic acid (PSS) was taken to the forefront via commercialization that led to extensive investigations throughout the 1990s and 2000s because of their ability to be dissolved in common solvents as well as the improved stability of the doped systems [51].

Though, one drawback for conductive polymers has been the instability of the doped state when exposed to chemical and thermal stresses or external stimuli such as humidity or ultraviolet light that can rapidly decrease their level of electronic conductivity.

This is one of the main reasons they have been unable to act as a complete alternative to Indium Tin Oxide (ITO) but rather they have been utilized in the past as a thin coating over Indium Tin Oxide for improving charge injection in Organic Light Emitting Diode (OLED) applications because they can continue electrical conductivity when cracks are formed in Indium Tin Oxide (ITO) films via their utilization as a conductive smoothing layer to reduce the film roughness.

They are also realized to smoothing the surface roughness of other materials such as silver nanowires with minimal effect on their conductivity. Other major issues for devices that demand low sheet resistance (R_s) include the blue/green trace the poly (3, 4-ethylenedioxythiophene) poly (styrene sulfonate) / Polyaniline (PEDOT: PSS/PANI) films exhibit respectively when applied hence they are desirable for display applications [4].

2.2.2 Carbon nanotubes

For Carbon Nanotube (CNT) thin films, large resistance is known to occur between overlapping Carbon Nanotubes (CNTs) known as junction resistance. Thus, longer Carbon Nano Tubes (CNTs) will be much desired since there will be less junction resistance between a small number of Carbon nanotubes (CNTs) junctions per unit area of film compared to a smaller Carbon nanotube (CNTs) on a film area that will have several overlapping Carbon nanotubes (CNTs) that will eventually result in larger junction resistance, but longer Carbon nanotubes (CNTs) are known to be hard to suspend in an ink. Such resistance has a restraint on the transport properties of Carbon nanotube (CNT).

Smaller Carbon nanotube (CNT) bundles will lead to higher conductivity than a larger bundle because if a larger bundle is utilized, inner tubes may not contribute to the current carrying capacity because of partial blocking from electrical contact with the overall network [69].

The major inhibition to Carbon nanotubes (CNTs) is the inability to achieve bulk quantities of the material with purity at an expected level for device stability. Impure materials might result in defects hence degrade device performance. Factors such as high purity, longer lengths (10-20 micrometre (µm) and proper ink suspension during growth will need major improvements to match ITO [4].

2.2.2. Graphene

Important challenges remain for Graphene when it is solution processed. Graphene is a two-dimensional allotrope of carbon. They comprise of a random network of overlapping graphene flakes which can be fabricated from solution. Though, one of the drawbacks of the flakes of graphene is that their layers consist of multiple boundaries and incorporate defects which affect conductivity because of the introduction of scattering sites that increase contact resistance [70].

Larger flakes are more desired for high performance applications with a single layer considered optimal since it will have no defects [4]. Though, since their properties are reliant on the size and number of graphene layers, better control is required for dispersing monolayers to obtain high performance when they are incorporated through a solution process, however, they are said to re-aggregate in solution into graphite flakes and the formation of continuous films of graphene is hard. This remains an interest, and improvement in this area would be highly advantageous in the future [5].

2.2.4. Nanomaterials

Nanoscale materials exhibit a great deal of promise because of their small scale on the order of 1-100nm which still shows high conductivity at small ratios as well as their tremendous optical properties [1]. They are on the nanoscales taking the form of different shapes and sizes with regards to metal grids, thin metal films, metallic nanowires, and nanoscale sheets of carbon such as Carbon nanotubes (CNTs) and graphene.

They can also be dissolved in solution; therefore, they can be made ultrathin via proper deposition techniques at low densities whilst still retaining high amounts of conductivity, transparency, and mechanical flexibility. These properties also make them appealing for printing techniques from solution [4].

2.2.5 Metallic nanowires and nanoparticles

Networks of metal nanowires have many benefits using growth techniques in solution that allow the fabrication of small diameter, long, (typically 40–200 nm with lengths of ~ 1–20 micrometre), smooth and highly pure nanowires because of their intrinsic metallic conductivity. Because of their varying lengths and diameters, they can be suitably patterned to suit their requirements on electronic devices [4].

Their morphology has intrinsic properties which contrast significantly from those of the bulk material because of their low-dimensionality and they have enormous prospects for scaled down device structures.
Silver is best suited for incorporation in nanowire structures because its high electrical conductivity which gives tremendous electrical transport and low optical absorption (for a metal).

Random nanowire networks can be cheaply deposited on films by solution-processable techniques such as drop casting, spin coating, spray coating, or rod-coating. All these methods are compatible with low temperature deposition processes and do not require any vacuum equipment [71].

With regards to a cost comparison between Indium Tin Oxide and silver, the difference in cost between both materials is not much from a bulk perspective but considering the amount of silver that will be used for a touch screen application, the quantity of silver needed is a lot less than Indium Tin Oxide. Other cost benefits in industrial fabrication include the use of low-cost equipment that need low temperatures with greater throughput and capacity for expansion using the roll-to-roll printing techniques contrary to highly expensive vacuum processes that require high temperatures [4].

2.2.6 Hybrid metallic nanomaterials

It is anticipated that single component electrodes can be effectively applied for better performance in electronic devices though the combination of each component material to form a composite may provide symbiotic properties that may give rise to greater benefits than the single components acting alone, as mentioned earlier the use of poly(3, 4-ethylenedioxythiophene)poly (styrene sulfonate) (PEDOT:PSS) and Carbon nanotube (CNT) may provide smoother surface that reduce contact resistance between overlapping Carbon nanotube (CNT) thus providing continuity in their conducting paths for enhanced electrical stability [72].

Also, the embedding of Carbon nanotubes (CNTs) with either Silver (Ag) or Gold (Au) nanoparticles may provide additional electrical conductivity, either through conduction via the metal nanoparticles, or by potential doping of the Carbon nanotubes (CNTs) [9].

2.2.7 Organic-inorganic nanocomposites

Nanocomposites can be mixed on the nanoscale, to combine the properties of two or more different materials with the prospect of novel mechanical, electronic or chemical behaviour development. The mixing of nanoparticles with an aqueous or organic liquid to form a suspension or paste can be used to form thin film composite electrodes for integration into device components. They are easily synthesized since they have solubility properties [73].

There have been many chemical techniques that have been developed to prepare nanocomposites of metallic nanoparticles (NP) and conductive polymers. Overall, there are many routes that can be followed for their development: A ''one-pot' method can be followed whereby, the monomer or polymer acts as a reductant for the metal in this approach or the nanoparticles are prepared followed by dispersion of the nanoparticles into a polymer matrix or the chemical polymerization of monomeric groups on the surface of the nanoparticle. This can be done by simply mixing the two components (nanoparticle and polymer) in solution.

The most common synthesis of polymer hydrogel nanocomposite has been concentrated on structures utilizing poly (ethylene oxide), poly (acryl amide) or poly (vinyl alcohol) as the polymer. The polymer networks are cross-linked to form permanent covalent bonding and then swollen with water for incorporation of metal nanoparticles.

The embedding of the nanoparticles in the polymers can crosslink the hydrogel or attach to the chains of polymer and add new properties to the hydrogel by simply being embedded within the hydrogel network. There are distinct physical properties that are added by the Nanoparticles to the polymer hydrogels such as responsiveness to mechanical, optical, thermal, barrier, sound, magnetic, electric stimulation. These distinct properties lead to applications in the fields of, optics, sensors, electronics, drug delivery, actuators, food-jelly, and other biotechnological areas [10].

The stability of these nanoparticles is extremely important during the fabrication of nanocomposites since their particles can aggregate during their synthesis therefore the size of these nanoparticles need to be monitored or controlled if necessary because nanoparticles of extremely small diameters can be greatly beneficial by providing reduced light scattering properties for applications in optical sensors for example. Their control in morphology in terms of size, shape and spatial distribution can provide the composite material with modulated optical characteristics [74]. Among these materials, metal nanostructured silver nanowires (NWs) composites are known as the most encouraging candidates for the replacement of Indium Tin Oxide because of their excellent photoelectric performance, compatibility with flexible substrates and easy adaptation to large-scale fabrication. Several researchers have reported applications of silver NW transparent electrodes in thin-film solar cells, organic light emitting diodes, touch panels, fuel cells and stretchable electronic devices.

Chapter 3

3. Methodology: Development and optimization of polyvinyl alcohol (PVA) / silver nanowire (AgNW) composites

Chapter 3 describes the experimental techniques and methodology used, including the materials, fabrication methods, and characterization of Organic Field Effect Transistors (OFETs) and capacitors.

3.1. Polyvinyl alcohol (PVA) / silver nanowire composites: thin film morphology

Silver nanowires (AgNWs) thin films have emerged as promising next-generation transparent conductive electrodes (TCEs) and increasing the opto-electrical properties or long-term stability of silver nanowires (AgNWs) based transparent conductive electrodes (TCEs) is now a major research focus.

In the past decades, the fabrication of flexible and stretchable transparent conductive electrodes (TCEs) has attracted much attention because of their wide use in displays, touch screens, solar cells, and organic light-emitting diodes (OLEDs).

To date, the most utilized Transparent Conductive Electrode (TCF) material is indium tin oxide (ITO), which is usually sputtered on substrates by physical vapor deposition, with the resultant films known to have a high transmittance (over 90%) and a low sheet resistance (under $30\Omega sq^{-1}$).

Also, Indium Tin Oxide film is not appropriate for flexible applications and large area applications due to its high brittleness, high cost, and complicated processing conditions. The rapid development of new electronic devices is making a demand for novel materials to replace Indium Tin Oxide. A variety of candidates have been developed including conducting polymers, graphene, carbon nanotubes, and their hybrids. Among them, silver nanowires (AgNWs) are among the most promising candidates because of their excellent conductivity, superior optical properties, flexibility, and compatibility with large-scale manufacturing.

Huge advancements have been made by researchers around the world for silver nanowires (AgNWs) based Transparent Conductive Electrodes. Yet, there remain many problems to deal with for the practical commercialization of silver nanowires (AgNWs) based Transparent Conductive Electrodes. Primarily, the high contact resistance at nanowire–nanowire (NW–NW) junctions greatly restrains the current delivery capability of silver nanowires (AgNWs) thin films. Several strategies have been created to improve the conductivity of silver nanowires (AgNWs) thin films, including thermal annealing. [68]

Thermal annealing is an effective method to form fused contacts between nanowires which drastically reduces their electrical resistance. The occurrence of local sintering is the driving force of such an evolution of the electrical properties. From the experiments carried out, we observed that the sheet resistance is improved by the annealing process which might also mean that the surface roughness of the silver nanowires was reduced.

Annealing is carried out to a certain degree under nitrogen without melting the material to form fused contacts. Local sintering is said to occur because the atoms in the materials can diffuse across the boundaries of the particles, therefore fusing the particles together to form a solid network. However, there is a thermal limit to which the metallic nanowires can withstand. Further heating can make them unstable [67].

Fundamentally, the resistance of the silver nanowire network increases as the length and diameter of the nanowires used decreases [66]. The increase in resistance as their diameter reduces can be attributed to a phenomenon whereby as the diameter reduces close to or below the mean free path of electrons of the bulk material, surface scattering of the electrons occur which lead to a reduction of their mean free path subsequently increasing the resistivity above that of the bulk [16]. The length of the nanowire is however dependent on the percolative nature of the conduction mechanism in nanowire networks whereby several conducting paths can be generated with the use of longer lengths [66].

This report demonstrates the fabrication of an optimized silver nanowire thin film as a transparent conductive gate electrode for Organic Field electronic devices (OFETs) with reduced sheet resistance, reduced surface roughness, higher transparency and also the fabrication of a high k (k – refers to a material with high dielectric constant) dielectric material commonly known as Polyvinyl alcohol (PVA) for the fabrication of low voltage organic field electronic devices (OFETs) and capacitors through a low cost solution process.

In this experimental research, a spin coating method is used for fabricating silver nanowire and Polyvinyl alcohol (PVA) films on glass substrates to achieve more uniformity across the film. A composite film comprising of the silver nanowire network and polyvinyl alcohol was then fabricated by a lamination technique.

Spin-coating has widely been used as a deposition method due to its ability to form uniform films over large area and its applicability in large-scale production. The thickness of each layer was controlled by varying the concentration of solution and the spin-speed of the spin- coater. Spin coating is another cheap and fast method to produce homogeneous layers.

Figure 3.1 illustrates a spin-coating process. An excess amount of the dispersion is placed on the substrate, which is then rotated at high speed to spread the fluid by centrifugal force. The film thickness can be adjusted by varying the rotation speed, the rotation time, and the solid concentration of the dispersion.

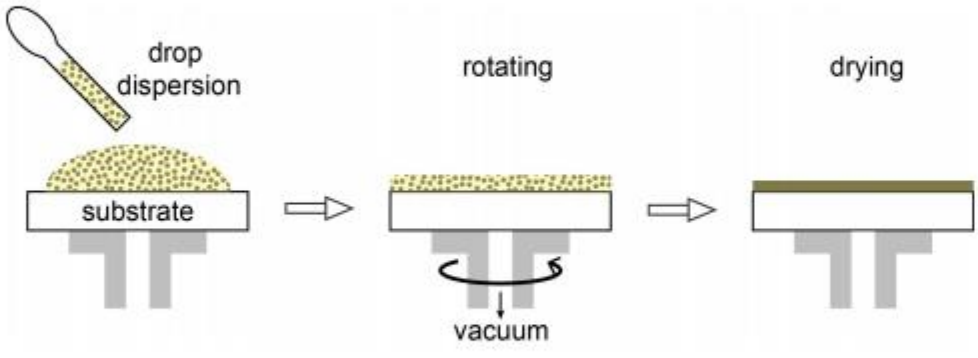


Figure 3.1: A schematic of the spin coating process.

3.1.1. Formulation of Silver nanowires dispersion

Silver nanowires (AgNWs) were purchased from Seashell Technologies as supplied with a concentration of 5 mg/ml in isopropyl alcohol (IPA). The mean length of the nanowires was 19.6 micrometer (µm) with a mean diameter of 23 nanometre (nm) as provided by the supplier.

The silver nanowires tend to dry on the walls above the liquid level and they also settle overtime which subsequently leads to agglomeration of the silver nanowires and a huge surface roughness when films of silver nanowires (AgNWs) are deposited. To prevent agglomeration, their content was shaken thoroughly until a homogenous solution was obtained and visually inspected to ensure the nanowires were in suspension before depositing the material on glass substrates to obtain a smooth thin film.

Dilution immediately before spin coating also helps to disperse the agglomerated silver nanowires but when left overtime they still settle and form clusters. The dispersion was further diluted by a factor of 1:4 with isopropyl alcohol, deposited with a pipette immediately onto a clean 2cm by 2cm glass substrate and then subsequently spun with a spin coater at a high velocity to centrifugally spread the solution over the substrate and make the surface smoother.

It was also realized that, at higher concentration of a silver nanowire solution as shown in figure 3.1.2, huge surface roughness and lower transmittance was obtained but the higher the conductivity and vice versa, hence a compromise had to be met.

An optimized solution with lower concentration of a silver nanowire solution (Diluted in 1:4 ratio) (as shown in figure 3.1.2.1) was developed and spin cast to reduce the surface roughness but still obtain an acceptable transmittance and conductivity.

3.1.2. Fabrication of a silver nanowire (AgNW) / polyvinyl alcohol (PVA) composites

To fabricate a composite, the silver nanowire (AgNW) dispersion was spun on a cleaned glass substrate at room temperature to obtain a uniform thin film of silver NW networks.

The conditions used to spin coat the silver nanowires were 1500rpm for 15 secs, and to form a fused contact at the silver nanowire (AgNW) junctions (i.e., reduce sheet resistance), the deposited silver nanowire network on glass was annealed for 5 minutes under nitrogen).

A Poly Vinyl Alcohol (PVA) thin film with the thickness of approximately 6µm was formed on a second glass substrate through the spin-coating method. Poly (vinyl alcohol) (PVA) was purchased from Sigma Aldrich, (Molecular weight, M_w = 89,000 – 98,000 99+% hydrolysed).

A 11% w.v (weight to volume ratio) solution of high molecular Poly Vinyl Alcohol (PVA) was prepared by measuring out 0.33g and adding this slowly to a beaker containing 3ml of water, with stirring. The mixture was heated at 100 degrees centigrade, stirring occasionally until the solution was clear to avoid boiling the solution. The solution was then deposited on a clean glass substrate to form a thin Poly Vinyl Alcohol (PVA) film via the spin coating method. Subsequently, the finished silver nanowire (AgNW) film was inverted and placed on the Poly vinyl Alcohol (PVA) film.

The silver nanowire (AgNW) network could be totally transferred onto the surface of the Poly vinyl Alcohol (PVA) film using an enough pressure.

Before transferring, the Poly vinyl Alcohol (PVA) film was pre-heated on a hotplate to soften the Poly Vinyl Alcohol (PVA) and make the transfer of silver nanowire (AgNW) networks easier by annealing the Poly vinyl Alcohol (PVA) film under nitrogen atmosphere at 95 degrees centigrade initially for 1 hour and thereafter at 75 degrees for 1 hour to remove any traps and increase the crystallinity due to increased hydrogen bond formation between the OH groups of Poly Vinyl Alcohol (PVA) caused by the increase in chain proximity and the chain mobility at the annealing temperature.

Finally, the upper glass substrate of the silver nanowire (AgNW) film was naturally peeled off, hence the silver nanowire – Polyvinyl Alcohol (Ag NW–PVA) composite film was well fabricated and measured.

An average sheet resistance of 104 ohm/square was obtained across the film and an average transmittance of 80% was obtained. (The transmittance of the films was measured using a spectrophotometer. Transmittance measurements were taken over the light visible region (wavelength of 400-700nm). The Sheet resistance was measured with a 4-point probe. The conditions used to spin coat the silver nanowires were 1500rpm for 15 secs, Anneal for 5 minutes under nitrogen).

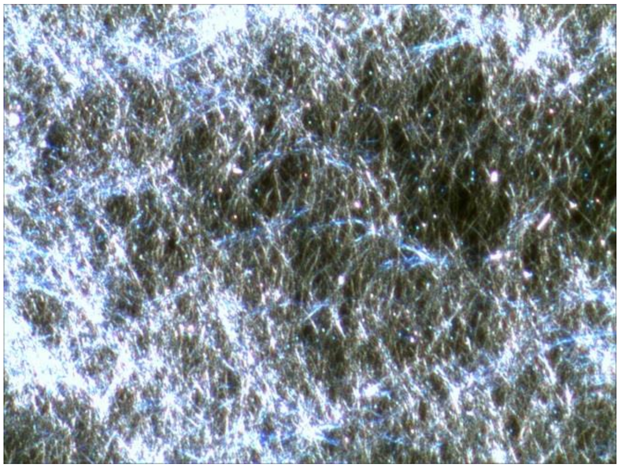


Figure 3.1.2. Microscopic images of deposited pristine silver nanowires (high concentration of AgNWs) on glass substrates from its original concentration (spin speed: 1500rpm for 15 secs, Annealed at 80 degrees under nitrogen for 5 minutes). Magnification X50.

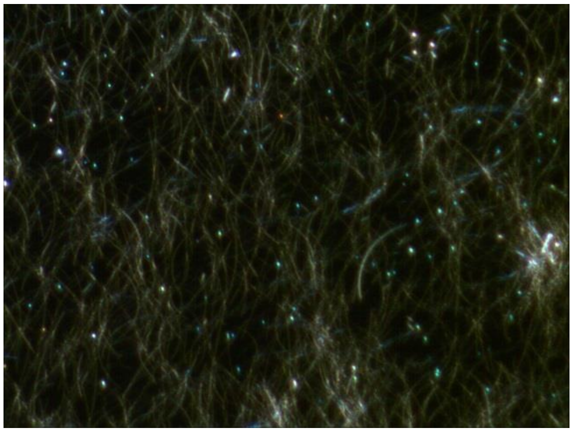


Figure 3.1.2.1. Microscopic images of deposited 1:4 dilution of silver nanowires (100 microliter of silver nanowires mixed with 400 microliters of isopropyl alcohol, properly shaken, and dispersed by spin coating deposition technique on a glass substrate) (lower concentration of silver nanowires) (Spin speed: 1500rpm for 15 secs, Annealed at 80 degrees under nitrogen for 5 minutes). Magnification X50.

3.2. Polyvinyl alcohol / silver nanowire composite films: performance (sheet resistance and transmittance)

In this study, a spin-coating method is used for producing silver nanowire (AgNW) films and Polyvinyl alcohol (PVA) films on glass substrates.

To improve the inherent, poor uniformity in conductivity and lower the high surface roughness of silver nanowire films, a composite film based on a silver nanowire network and polyvinyl alcohol was fabricated by a lamination technique. A transmittance of 80% with a sheet resistance of 104 Ωsq^{-1-}were measured for the silver nanowire–polyvinyl alcohol (AgNW-PVA) film.

The sheet resistance was measured using a four-point probe to measure voltage difference and the data reading were extracted from a Keithley source meter. Also, the transmittance was measured using a spectrophotometer. Transmittance measurements were taken over the light visible region (wavelength of 400-700nm).

3.2.1. Sheet Resistance

The most critical characteristics of a transparent electrode are its sheet resistance and transmittance. The sheet resistance is the unit of measurement when measuring the resistance of a thin film:

$$R_s = \frac{\rho}{t} \qquad (eq. 1.16)$$

Where R_s is the sheet resistance, t is the thickness of the film, and ρ is the resistivity of the film, $\rho = 1/\sigma$; σ is the d.c. conductivity. For a rectangular film of length L and width W, the resistance, Rs;

$$R = \frac{\rho}{t} \times \frac{L}{W} = R_s \times \frac{L}{W} \qquad (Eq. 2.7)$$

L/W is the number of squares of side W that can be covered on the film substrate without coinciding. Therefore, even though R_s has a unit of ohms as R does, it is generally quoted in "ohms per square because it is equal to the resistance between two electrodes on opposite sides of a theoretical square. The size of the square is unimportant.

However, in a sheet resistance measurement, several resistances need to be considered as shown in Figure 3.2.1. The probe has a probe resistance R_p. At the interface between the probe tip and the thin film, there is a probe contact resistance, R_{cp}. When the current flows from the small tip into the thin film and spreads out in the thin film, there will be a spreading resistance, R_{sp}. Finally, the thin film itself has a sheet resistance R_s.

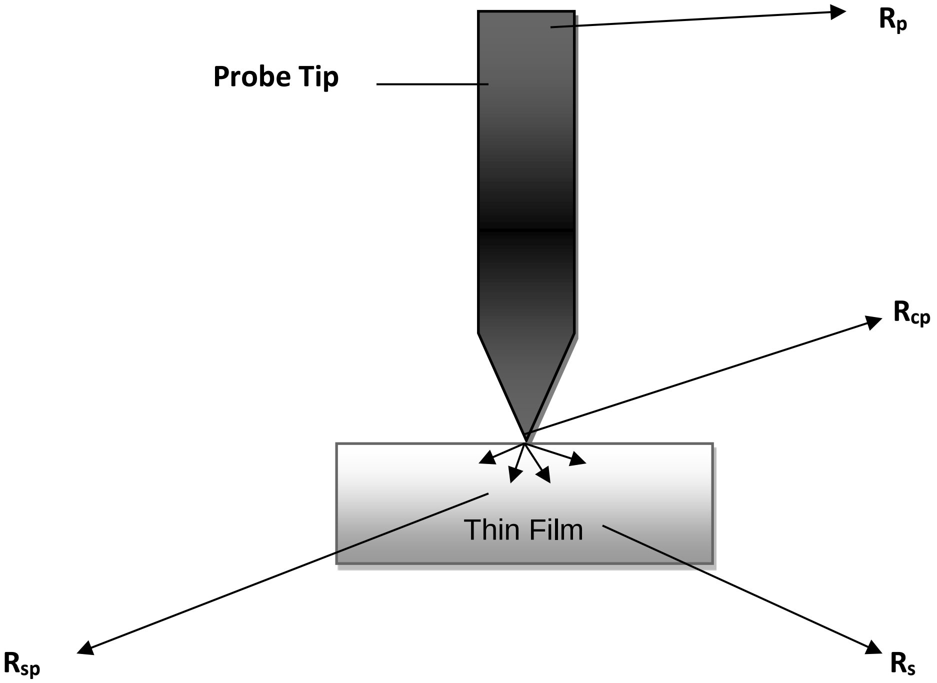


Figure 3.2.1. Several resistances in a thin film measurement when using a probe.

In a 2-point probe measurement, we measure the voltage that develops across the resistance by dividing the measured voltage by the sourced current. A problem that occurs when using a 2-wire setup is that the voltage is measured not only across the resistance in question, but also includes the resistance of the leads and contacts. Although the two-point probe method can calculate the resistance measurement, the four-point probe method is more accurate due to the use of two additional probes.

In contrast to the two-point method, the four-point method uses the two additional probes to measure the voltage potential of the material surface. Because a second set of probes is used for sensing and since negligible current flows in these probes, only the voltage drop across the film is measured. As a result, the sheet resistance measurement is more accurate, therefore a Four-point Probe measurement method was used in this research. The diagram for the measurement of sheet resistance by using the four-point probe is shown in Figure 3.2.1.1.

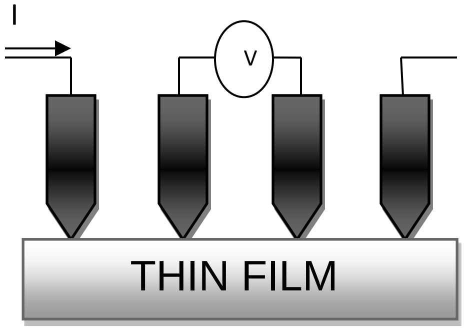


Figure 3.2.1.1. 4-point probe setup on a substrate.

Two probes carry the current and the other two probes sense the voltage. The four-point probe technique involves bringing four equally spaced probes in contact with a material of unknown resistance. The probe array is placed in the centre of the material, the two outer probes are used to source current while the two inner probes are used to measure the resulting voltage difference across the surface of the material. Sheet resistance of the electrode was measured with a 4-point probe machine using a Keithley 2400 source meter to supply current and sense the voltage. In the four-point probe setup the sheet resistance is measured by sending current through the outer two probes and consequently pressing down on the stage of the machine until slight contact has been made by the film and the probe tips.

3.2.2. Transmittance

The transmittance of the films was measured using a spectrophotometer, where the detector is placed behind the thin film in-line with the source of the light. A broadband source was used as a light source. The set up used is shown below in figure 3.2.2. When light hits the film, the incident light can be transmitted, absorbed, or reflected by the object. The ratio of transmitted light to the incident light is defined as transmittance of the object, which is usually shown in percentages.

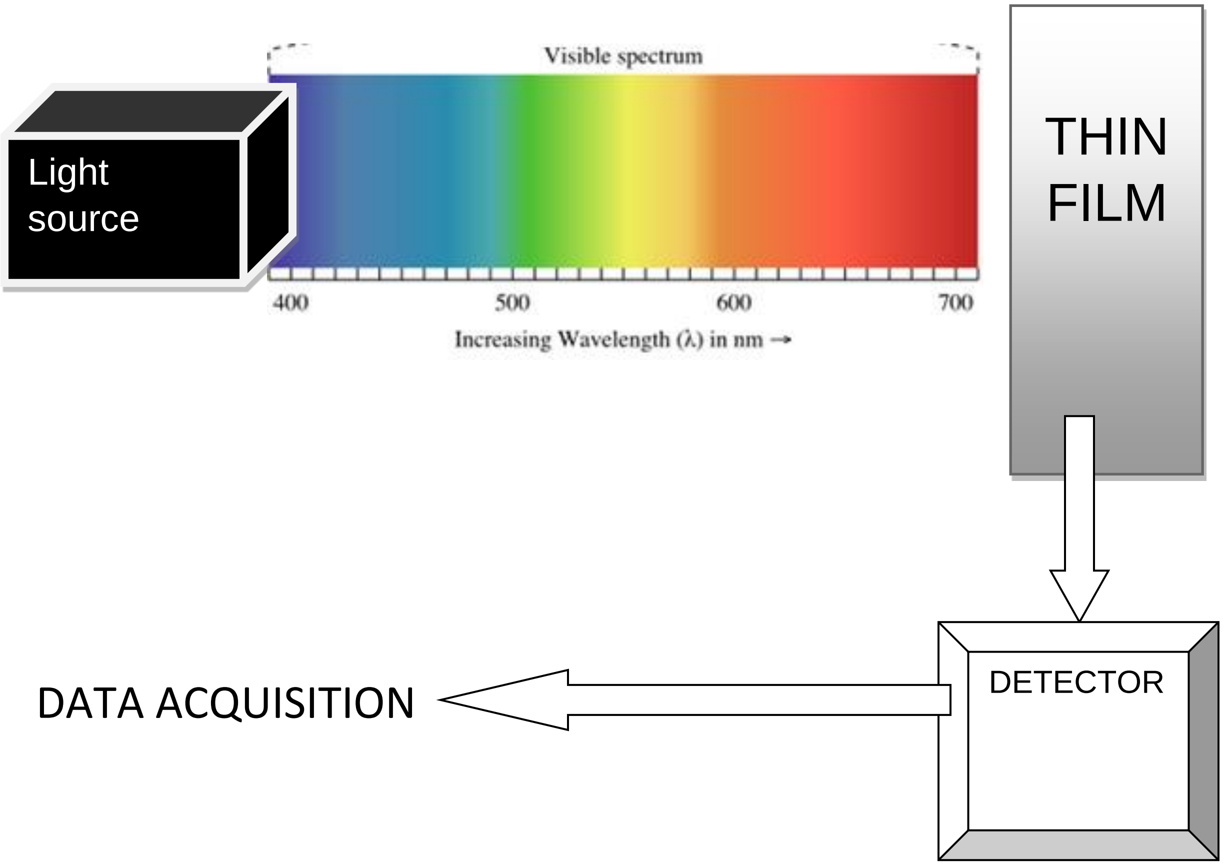


Figure 3.2.2. The set-up used to measure the transmittance of the studied films.

Reference measurements of clean glass substrates were measured to ensure a calibrated system set up. Also, the transmittance of an object can vary in response to the wavelength of the incident light.

The transmittance was measured with a light source coupled through an optical fibre to a detector. A tungsten halogen lamp (LS-1TM) from Ocean Optics guided by a fibre was employed as the light source.

Two detectors, Indium Gallium Arsenide (900 to 2500nm) and Silicon CCD Array (400 to 1100nm) were used to obtain the transmittance at a wider range of wavelengths. In this report, the samples were placed orthogonal to the incident light.

Transmittance was calculated as the ratio of the light intensity detected when the thin film was placed under light, and the light intensity detected when the clean transparent glass slide was placed under light as point of reference to determine their transmittance ratio as a form of percentages (%).

Transmittance measurements were taken over the light visible region (wavelength of 400-700nm).

3.3. Determination of capacitance using aluminium as bottom metal electrode/Polyvinyl alcohol (PVA) as insulator / gold as top metal electrode

An Agilent Technologies' E5270B measurement mainframe connected with four E5287A source measure units connected to four Karl Suss PH100 micromanipulator probes was used to assess the characteristics of the Organic Field Effect Transistor devices.

The 9 Organic Field Effect Transistor (OFET) devices with variable channel lengths (20-100micron) are placed on the probe station sample holder and electrical contacts are made between the probes and device electrodes. 3 electrical contacts are made to establish a gate, source, and drain contact while 2 contacts are made on the top and on the bottom electrodes with one electrode grounded when measuring the capacitors.

Device basic parameters like mobility, threshold voltages, subthreshold swing and the on/off ratio were also calculated additionally for the transistor device.

To calculate the mobility, the square root of the drain current ($(I_D)^{1/2}$) is plotted against gate voltage (V_g) and then by fitting a straight line to the linear region of the curve, the value of the slope of the curve ($|I_D|^{1/2}$ against V_g) is found and then substituted into the simplified equation (Eq. 1.7) which was deduced from the characteristic equation for an Organic Field Effect Transistor (OFET) in the saturation regime to obtain the value for the mobility.

3.4. Fabrication and characterization of parallel plate capacitors

Capacitors are one of the essential, dominant passive components with many applications and properties, including filtering, timing, A/D (alternating/direct) current conversion, termination, decoupling, and energy storage. In its simplest form, a capacitor consists of two parallel conducting electrodes of area *A* separated by a dielectric at a distance *d*. Applying a voltage (v) to the electrodes creates an electric field (*E*) between them and charge (Q) is stored on each of the conducting plates. The plate with positive charge is called the anode, while the plate with positive charge is referred to as the cathode.

The amount of charge (in coulomb) stored in a capacitor is linearly proportional to, the electric potential difference (in volt) applied between the two plates: where C is a positive proportionality constant called capacitance. Physically, capacitance is a measure of the how much electric charge is stored between the two parallel plates of the capacitor for a given potential difference created across the capacitor

Capacitance is directly proportional to the area *A* of the conductive plates and inversely proportional to the distance *d* between them. In real capacitors, the spacing between the two conductive plates is filled with a dielectric material.

3.4.1. Experimental details:

(i) Corning glass slides were used as a substrate and cut into 1cm-by-1cm size. The glass slides were cleaned with acetone, methanol, and isopropanol baths in the sonicator for 5 minutes each and immediately dried with a nitrogen gun.

(ii) **Bottom electrode (Aluminium or Silver nanowires (AgNWs)**: A thin layer of Aluminium was evaporated using a turbo pump evaporator on corning glass substrates to serve as bottom gate electrodes to obtain a thickness of 80nm. For the case of silver nanowires (AgNW) based Organic Field Effect Transistors (OFETs), the optimized solution with lower concentration of a silver nanowire solution (Diluted in 1:4 ratio) was spin coated on 1cm-by-1cm glass substrates (Spin speed used was 1500rpm for 15 secs, annealed at 80 degrees under nitrogen for 5 minutes) then this can be utilized as a bottom electrode.

(iii) **Dielectric deposition (Insulator)**: Poly (vinyl alcohol) (PVA) was purchased from Sigma Aldrich, (M_w = 89,000 – 98,000 99+% hydrolysed). 1 w.t% - 11 w.t% solution of high molecular Poly Vinyl Alcohol (PVA) was prepared using the same procedure that was adopted when making the dielectric for the transistors.

The mixture was heated on a hotplate at 100 degrees centigrade, stirring occasionally until the solution was clear. Once dissolved, the solution of Poly Vinyl Alcohol (PVA) at various w.v (weight to volume) percentages was deposited via spin coating method at 1500rpm for 15secs to obtain a film on different samples with sputtered Aluminium as the bottom electrode.

The film is placed on a hot plate and annealed under nitrogen atmosphere at 95 degrees centigrade initially for 1 hour and thereafter at 75 degrees for 1 hour to remove any traps and increase the crystallinity due to increased hydrogen bond formation between the OH groups of Poly Vinyl Alcohol (PVA) caused by the increase in chain proximity and the chain mobility at the annealing temperature. The thin film is then allowed to cool down to room temperature before finally depositing the top electrode (Gold).

(iv) **Top contact electrode deposition:** Top contact electrodes using gold metal were finally evaporated on top of the insulator (Polyvinyl Alcohol) (PVA) through a mask with area 0.012cm^2 rectangular patterns to form the top electrode.

Nine (Metal – Insulator – Metal) capacitors were fabricated and measured for various dielectric (Polyvinyl Alcohol (PVA) weight by volume ratios (w.v %) (1% -11%) to understand the effect, varying the concentration of the dielectric Polyvinyl Alcohol (PVA) w.v % (dielectric thickness) has on its capacitance and the charge carrier mobility of the transistor devices. The effect of changing the frequency (from 1 kHz to 1MHz) on the capacitance of the dielectric at 11% Poly Vinyl Alcohol (PVA) w.v concentration was also investigated. Probe contacts are made on the top and on the bottom electrodes with one electrode grounded when measuring the capacitors.

The capacitance is measured at a frequency range, 1kHz-2MHz, the values of capacitance measured for various dielectric (Poly Vinyl Alcohol (PVA) weight by volume ratios (1% -11%) are plotted and displayed in the figures below. A capacitance of 1 nano farad (1nF) was achieved for (Polyvinyl Alcohol (PVA) with 11% w.v and a thickness of 6 micrometre was measured. This concentration was used to fabricate most of the Organic Field Effect Transistors (OFETs) in this research. Other capacitance values for different concentrations are shown in figure 3.3 below.

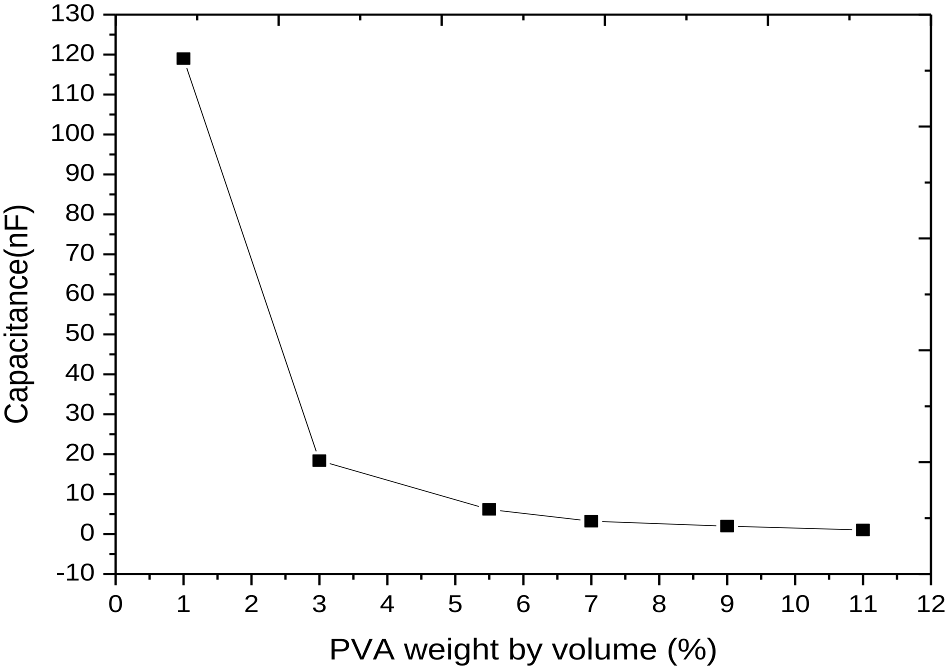


Figure 3.3. Relationship of the measured capacitance depending on the different PVA concentrations (weight by volume) (1-11%), i.e., PVA film thicknesses.

Chapter 4

Fabrication of high and low voltage Organic Field-Effect Transistors (OFETs)

Organic field-effect transistors (OFETs) have drawn much attention owing to their vital applications in large-area, low-cost, and/or flexible electronics. Great efforts have been dedicated to improving the performance of Organic field-effect transistors (OFETs). For Organic field-effect transistors (OFETs), lowering the operating voltages is pursuit of the goal because, to date, the operating voltages still are relatively high, which may lead to high power consumption in organic circuits.

As described in Chapter 1, the operating voltages can be successively reduced by increasing the dielectric capacitance per unit area of the gate insulator by decreasing the thickness of insulator or/and using the high dielectric constant (K) dielectric. The former has been improved by utilizing self-assembled layer and polymer thin film as insulators. However, decreasing the thickness of the dielectric might lead to leakage currents, therefore care needs to be taken. The common high-K dielectric is inorganic metal-oxides in general. Up to now, it still is of great importance to develop novel high-K materials as gate insulator, especially organic high-K dielectric. Ideally, to be power efficient, Organic field-effect transistors (OFETs) are operated with gate voltages as low as possible. To fulfil this requirement, low values of transistor threshold voltage (V_T) and subthreshold swing (SS) are essential. Ideally, threshold voltage (V_T) should be around 0 V and Subthreshold swing (SS) close to 60 mV/dec, which is the theoretical limit of subthreshold swing at 300 K. [75]

In this chapter, our approach from High voltage towards low voltage operated OFETs is described. The reduction of operational voltage was achieved by the introduction of high capacitance insulators, introduction of higher K insulators/dielectric and improvements in morphology of active layers obtained via dielectric surface modifications for example the use of Self assembled monolayers. High capacitance was attained using ultra-thin films of SiO_2 and high- K dielectrics such as Aluminium oxide (Al_2O_3) and Polyvinyl alcohol (PVA). In some cases, insulator surfaces were modified by addition of an extra dielectric coating between the main insulator and semiconductor using self-assembled monolayers (SAMs). The fabricated transistors display relatively lower leakage, lower threshold, smaller hysteresis, good carrier mobility, high gate capacitance, and exceptionally low inverse subthreshold slope.

4.1.1. High voltage OFETs using SiO_2 as dielectric - Device fabrication

In order to investigate the operation mechanism of transistors from a practical sense, basic Bottom gate/Top-contact (BGTC) organic thin film transistors on Silicon substrate/ Silicon dioxide (SiO_2) as dielectric (K = 3.9) and using poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) ; a polycrystalline semiconductor which was synthesized in chemistry, (University of Manchester) as the semiconductor layer was fabricated and their performance was characterised.

Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) is a polycrystalline semiconductor with exceptionally high saturation mobility in some device configurations (up to 10cm^2 /V.s) . Its Highest Occupied Molecular Orbital (HOMO) level is found at -5.2eV with the Lowest Unoccupied Molecular Orbital (LUMO) at -3.5eV. The dielectric was treated with a Self-assembled Monolayer (SAM) known as ODTS (Octadecyl trichlorosilane) to enhance performance.

Top contact and bottom contact structures were fabricated to compare the performance of both structures. In the top-contact structure the source and drain electrodes (Au) were deposited on top of the semiconductor, whereas, in bottom-contact devices the semiconductor was deposited on top of the source/drain electrodes and dielectric. The figure 4.1.1 shows the schematic of both structures.

Figure 4.1.1. Schematic showing top (left) and bottom (right) contact OFET structures.

4.1.2. Experimental: Fabrication of Top contact and Bottom contact OFETs

Substrate preparation: Initially, the silicon/silicon dioxide substrate was cut into 2cm-by-2cm sizes which were cleaned with acetone and methanol in a bath using the sonicator. The substrates were blown dry with nitrogen air gun. SAM (Self assembled monolayer) was prepared by mixing 4.5µl (microliter) Octadecyl trichlorosilane (ODTS) in 4ml of Trichloroethylene and then deposited by spin coating method on top of the dielectric layer to treat the surface by adding wettability, improve carrier mobility and reduce tunnelling current density (low leakage current). The sample was then annealed at 105 degrees for 20 minutes.

Semiconductor and Metal components: The semiconductor (Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c] pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) was weighed (2.5mg) and dissolved in 0.5ml of Dichlorobenzene (DCB) solvent at a temperature of 120 degrees on a hot plate. The Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c] pyrrole-1,4-dione)thieno[3,2-b]thiophene) PDPPTT was deposited by spin coating on top of the Si/SiO2/ODTS modified surface and annealed at 120 degrees for 30 minutes. Shadow masks were placed on the sample to pattern the electrodes.

The sample was taken and placed in the evaporation chamber where Gold (Au) was thermally evaporated at 60nm thickness with channel lengths (20-100micrometer) and widths of 1000micrometer, respectively.

15 devices were fabricated on the sample. Measurements were then taken for this device using a 3-point probe setup. The Silicon dioxide was scratched off carefully at the edges to punch through with the probe to establish contact with the gate (Silicon).

Measurement: To determine the carrier mobility and the threshold voltage, Gate voltage (V_G) and Drain voltage (V_D) were driven at the same values and the square root of the drain current (I_D) was plotted against $V_G = V_D$. The measured hole mobility, μ, and threshold voltage, V_T, were obtained from the slope and intercept of the $(I_D)^{½}$ vs V_{GS} curve as shown in figure 4.1.2b for example. The figure 4.1.2a shows the transfer characteristics of the Organic Field Effect Transistors (OFETs).

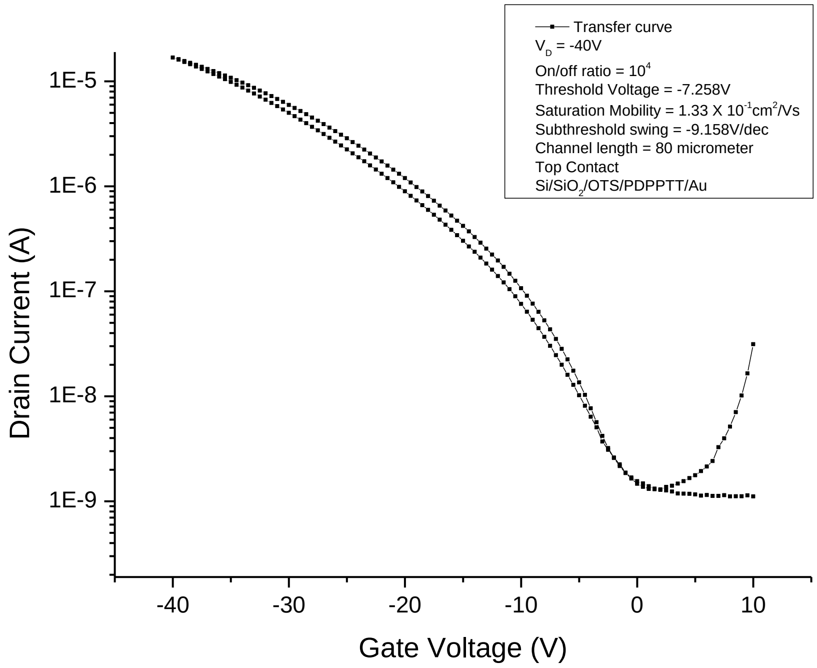


Figure 4.1.2a. A representative transfer characteristic for the top contact OFETs.

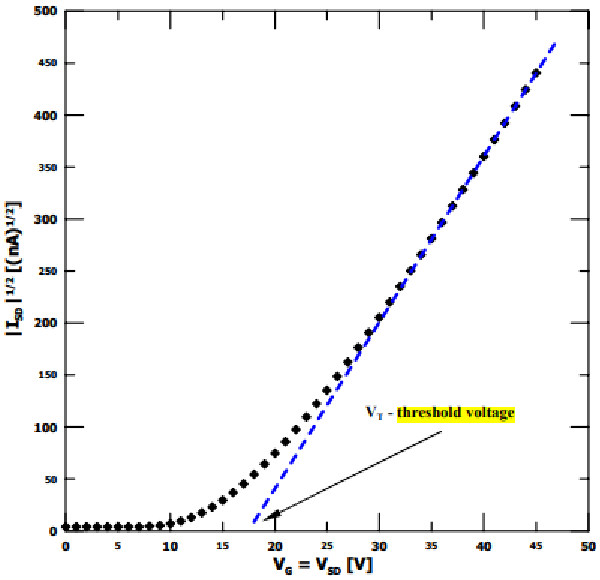


Figure 4.1.2b. $|I_{SD}|^{1/2}$ versus $V_G = V_{SD}$ for the determination of threshold voltage.

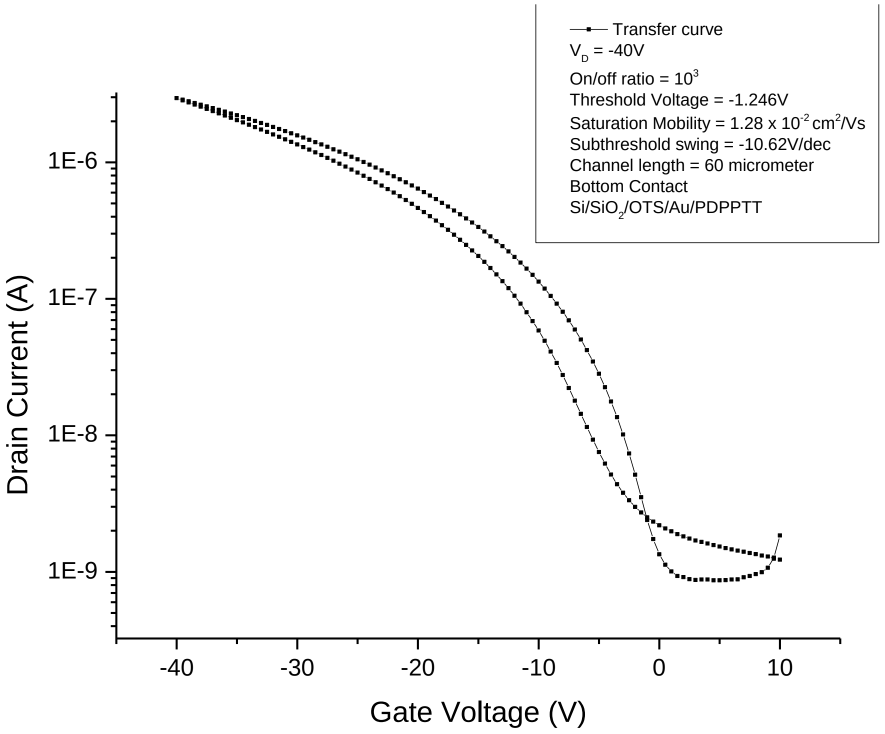


Figure 4.1.2c. A representative transfer characteristic for the bottom contact OFETs.

4.1.3. Results and Discussion

The top contact structure resulted in a charge carrier mobility of 1.33 x 10^{-1}cm^2/V.s due to the larger output current than the bottom contact (as shown in figure 4.1.2c) , which may be attributed to the small contact resistance that exists between the metal and semiconductor for efficient charge injection and transport while the bottom contact structure resulted in a charge carrier mobility of 1.28 x 10^{-2} cm^2/V.s due to a larger contact resistance or voltage drop at the source electrodes.

However, for this device that was made, the threshold voltage is quite large for the top contact structure. The better linearity of the Y-function provides greater reliability and better reflects the threshold of charge accumulation in the channel. This is not the case for this device, hence a larger threshold voltage as shown in figure 4.1.2a. Traps may be slowing down the accumulation of charges.

Also, a thinner dielectric or high k dielectric will be much preferred for better accumulation of charges and increased capacitance, however high k dielectrics have been known to cause large hysteresis due to high defect density and they may cause dipolar fields to the adjacent organic semiconductor that induce energetic disorder in the transporting carriers near the dielectric/organic semiconductor interface therefore degrading mobility of the organic field effect transistor.

A smaller threshold voltage is always preferred because it means that the operating voltage can be low. Hysteresis reflects the quality of the device, and it is characterized as the threshold voltage shift between the sweeping of the gate voltage (V_G) back and forth during which the strong electrical field affects the chemical bonds of the gate dielectric and organic semiconductor thereby creates defects such as traps.

These traps can capture charges for long periods of time; an explanation for this hysteresis may be due to trapping and migration of dopants in the organic semiconductor film that may be linked with moisture, impurities, and defects. The device was also left in air for some period; this may have led to these defects and the material used was stored for a long period of time.

The sub-threshold swing is also large for both devices. Typically, sub-threshold swing should be small for fast switching devices. It suggests how fast the channel switches on/off, it may also indicate a gate voltage reduced range span required to fully turn the channel on and off therefore suggesting ability to be operated at low voltages.

The sub-threshold swing is high due to many interface states that have been distributed at the dielectric/semiconductor interface. To decrease the sub-threshold swing, the dielectric may be made thinner to increase the capacitance or by applying a high k dielectric to reduce the weight of the surface state capacitances per unit area or the dielectric/semiconductor interface may be treated with a Self-Assembled Monolayer (SAM).

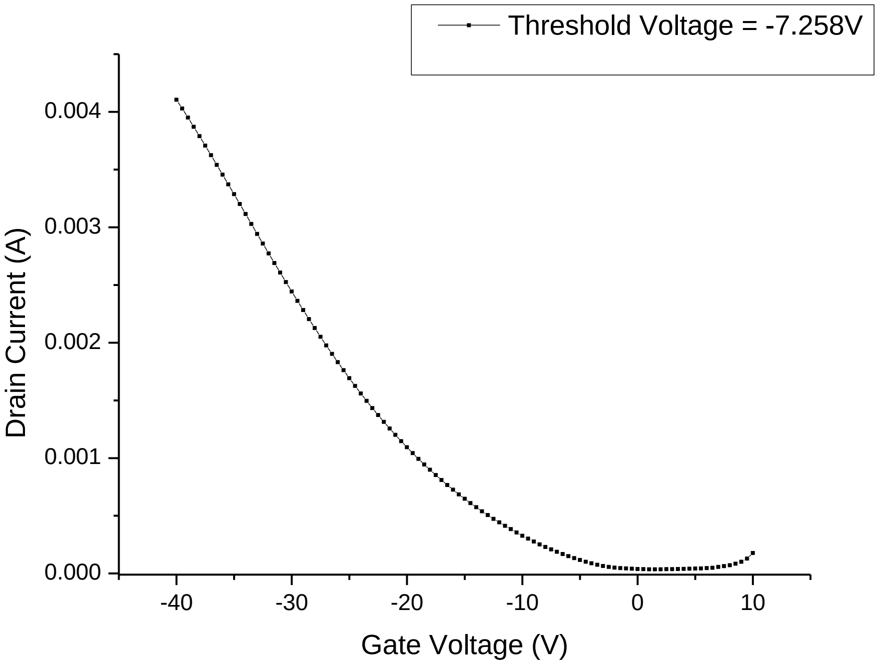


Figure 4.1.3. Drain current vs. gate voltage for the determination of the threshold voltage.

The diagram Figure 4.1.3.1 shows the transfer characteristics using the same structure for a device that was made when the material semiconductor was newly synthesized in which there may have been less trapping. As shown in the graph, the hysteresis is less than the one in the previous graphs which may be due to large doping. The threshold voltage is also low, and the sub-threshold swing is much better, as well.

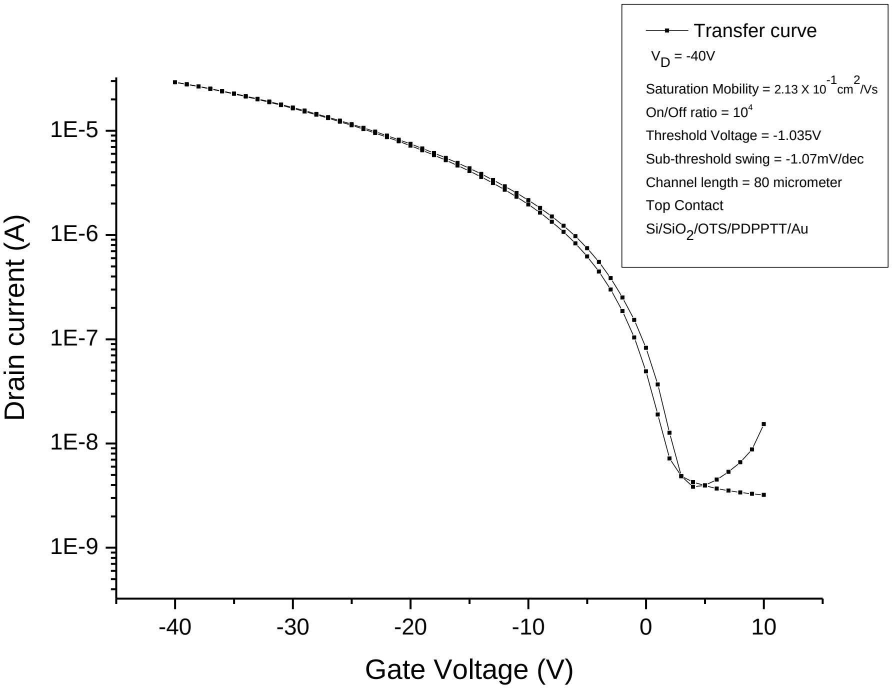


Figure 4.1.3.1. An example of OFET transfer characteristic with reduced I/V hysteresis.

The top contact structure exhibited a much better mobility than the bottom contact structure. High operating voltages (40V) were required to operate this device which is attributed to the thick conventional gate dielectrics (Silicon dioxide (SiO_2) that was used. To use a lower operating voltage, an alternative Organic Field Effect Transistor (OFET) structure consisting of a thinner dielectric and a higher K (K =9.9) (Aluminium as gate electrode; Aluminium oxide as dielectric; Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) as semiconductor and Gold (Au) as contact electrodes. (Al/Al_2O_3/PDPPTT/Au) was investigated.

4.1.4. Low voltage OFETs using aluminium oxide (Al_2O_3) – Device fabrication

The advances described in this section demonstrate a cheap fabrication of high performance, low voltage organic field effect transistors (OFETs) via the use of anodized aluminium oxide as the dielectric.

4.1.5. Experimental - Fabrication of OFETs using aluminium as gate electrode/Al_2O_3 as dielectric /PDPPTT as semiconductor/Au as contact electrodes

Glass substrates were cut into 2cm-by-2cm sizes and then cleaned with acetone and methanol in a bath using the sonicator. Aluminium (Al) was thermally evaporated on the glass substrate as gate electrode at thickness of about 250nm. Aluminium oxide layer (K =9.9) was grown by a technique known as anodization which is an electrochemical process that helps improve the natural oxide film and produces stable, highly resistant films.

The anodized aluminium layer is grown by passing a direct current through an electrolytic solution, with the aluminium object serving as the anode (the positive electrode). The current releases hydrogen at the cathode (the negative electrode) and oxygen at the surface of the aluminium anode, creating a build-up of aluminium oxide.

The evaporated Aluminium (Al) sample was placed in a solution of citric acid bath (electrolytic solution) and voltage swept up to 5V to pass current through. The thickness of Aluminium (thickness = 6.5nm) depends on the amount of voltage applied. The sample was washed in deionized water afterwards and blow dried. The sample was octadecyl trichlorosilane (ODTS) treated as done previously, and then the semiconductor (Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c] pyrrole-1,4-dione) thieno[3,2-b]thiophene) (PDPPTT) was deposited on top of the layer. Gold (Au) was thermally evaporated through a shadow mask as source/drain electrodes. The schematic (figure 4.1.4) shows the structure of the Organic Field Effect Transistor (OFET).

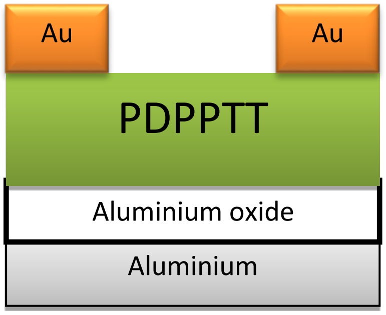


Figure 4.1.4. Schematic of a BGTC organic field effect transistor using aluminium oxide as gate dielectric and an organic semiconductor (PDPPTT) with source and drain electrodes (Au).

The devices were taken for measurement. The figure 4.1.5 shows the Transfer and leakage current characteristics of the OFETs.

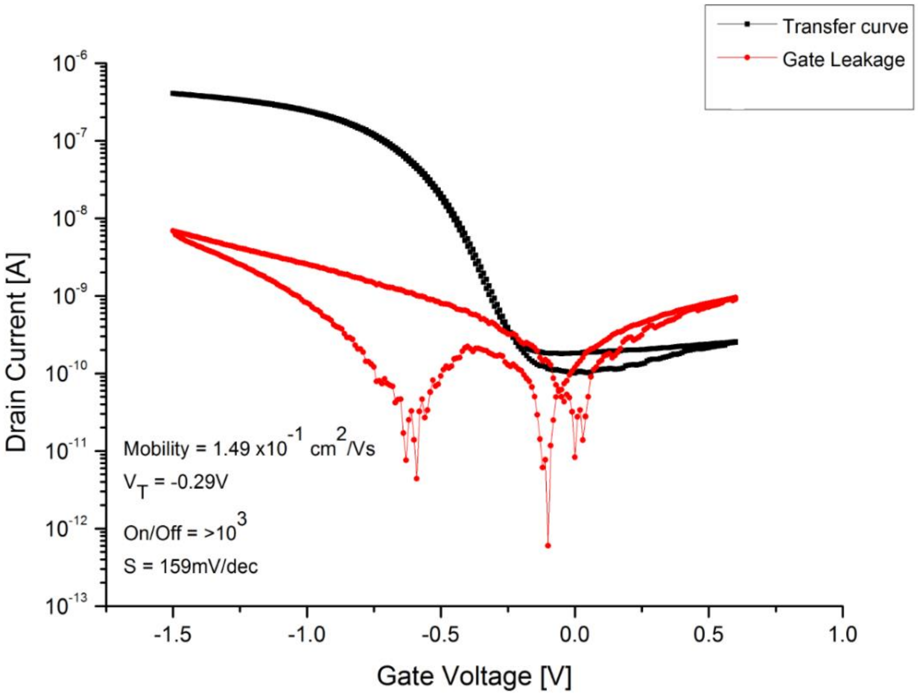


Figure 4.1.5. Transfer (black) and leakage current (red) characteristics for the OFETs.

4.1.6. Results and Discussion

A charge carrier mobility of 1.49 x 10^{-1} cm^2/V. s, threshold voltage of 0.29V and on/off ratio of 10^3 was obtained. The mobility is still low but low voltage operation has been established with a thinner and higher K dielectric (K =9.9). Transistor action is observed with low operational voltage of -1.5V attributed to the use of very thin gate insulators with high gate capacitance.

Most work has been done on devices that operate in p-type accumulation mode using p-type semiconductor(Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT), as most organic semiconductors to readily allow hole injection from gold source-drain electrodes and formation of a hole accumulation layer at the active interface.

In this report we have fabricated Silicon based transistors to investigate and understand the basics of operation in transistors. However, the advantage of organic electronics, independent of expensive rigid substrates, cannot be achieved with this system because with the use of thermally oxidized silicon wafers, the gate electrode (i.e., the wafer) cannot be patterned and they require high operating voltages for operation.

To follow the trend of reduced power consumption by employing low voltage, the use of a higher dielectric constant and thinner dielectrics than silicon dioxide was investigated. Another inorganic oxide such as Aluminium Oxide (Al_2O_3) was used in this report, to investigate the ability to operate these transistors at low voltages by using thinner high k dielectric materials such as Aluminium oxide on thin film transistors.

Another approach was the use of anodization to get thin film dielectrics in a solution-based approach. While most high permittivity materials suffer from expensive deposition methods (evaporation) and poor film quality (requiring relatively thick films to reduce gate leakage), the implementation of Aluminium Oxide (Al_2O_3) has made good progress, because of suitable deposition processes for Al_2O_3 and the direct conversion of Aluminium (Al) by anodization.

However, the Aluminium and Gold electrodes are still evaporated, so to incorporate fully a more flexible and cheaper process for the fabrication of electronic devices such as Organic Thin Film Transistors (OTFTs). Solution processed electrodes for these Organic Thin Film Transistors (OTFTs) are fabricated using silver nanowires as gate electrode and an organic polymer known as Poly (vinyl alcohol) PVA as the dielectric. The experiments carried out are detailed in the following sub chapters.

4.1.7 Low voltage OFETs using AgNWs as gate electrode and PVA as a dielectric

The advances described in this section demonstrate a cheap fabrication of high performance, low voltage organic field effect transistors (OFETs) via the use of Polyvinyl Alcohol (PVA) as the dielectric.

4.1.8. Experimental details:

Substrate Preparation: Glass slides were used as a substrate and cut into 2cm-by-2cm size. The glass slides were thoroughly cleaned with acetone and methanol in a bath using the sonicator and immediately dried with a nitrogen gun.

Gate Electrode preparation: A drop of silver paint was deposited at one of the edges of the glass substrate and left to dry to improve the contact with the bottom silver nanowire transparent conducting electrode that is to be deposited on top of it. Silver Nanowires in isopropanol (IPA) (silver nanowires (AgNWs) -25), Length 15-30um, Diameter 15-35nm, 5mg/ml concentration purchased from seashell were diluted with isopropanol (IPA) by a factor of 1:4. 400µl (microliter) of IPA was mixed with 100µl (microliter) of silver nanowires (AgNWs) in a vial bottle. The mixture was shaken thoroughly until a homogenous mixture was obtained. The solution was spin cast at 1500rpm for 40 seconds to allow the solvent to evaporate. The sample was annealed under nitrogen at a temperature of 140 degrees centigrade for 5 minutes to fuse the junctions in the silver nanowires

Dielectric preparation: Poly (vinyl alcohol) (PVA) was purchased from Sigma Aldrich, ((Molecular weight; M_w = 89,000 – 98,000 99+% hydrolysed). A 11 w.t% solution of high molecular Poly Vinyl Alcohol (PVA) was prepared by measuring out 0.33g and adding this slowly to a beaker containing 3ml of water, with stirring. The mixture was heated at 100 degrees centigrade, stirring occasionally until the solution was clear to avoid boiling the solution.

Metal and Semiconductor preparation: The Poly Vinyl Alcohol (PVA) solution was spin cast onto the Glass/silver nanowire sample at 1500rpm for 15 seconds and heated at 100ºC for 1 hour. Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene (PDPPTT) was spin cast onto the glass/silver nanowires (AgNWs)/Polyvinyl Alcohol (PVA) structured sample and annealed under nitrogen at 120ºC for 30 minutes. Gold was evaporated through a shadow mask onto the sample as a top contact to form source and drain electrodes. The figure 4.1.6 below shows the Glass/AgNW/PVA/PBDDTT/Au Organic Field Effect Transistor (OFET) structure.

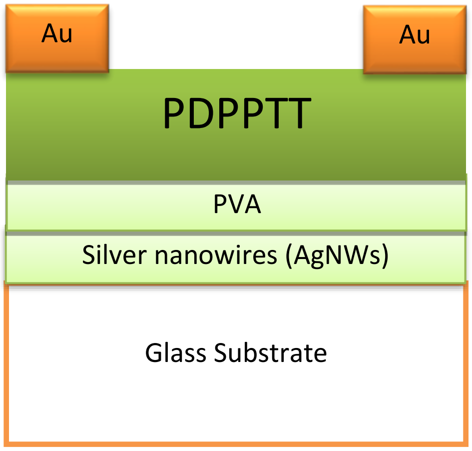


Figure 4.1.6. A schematic of the device structure using AgNWs as the gate electrode / PVA as the gate dielectric.

The devices were taken for measurement. The following figure 4.1.7 and figure 4.1.8 shows the transfer characteristics and leakage current of the Organic Field Effect Transistors (OFETs).

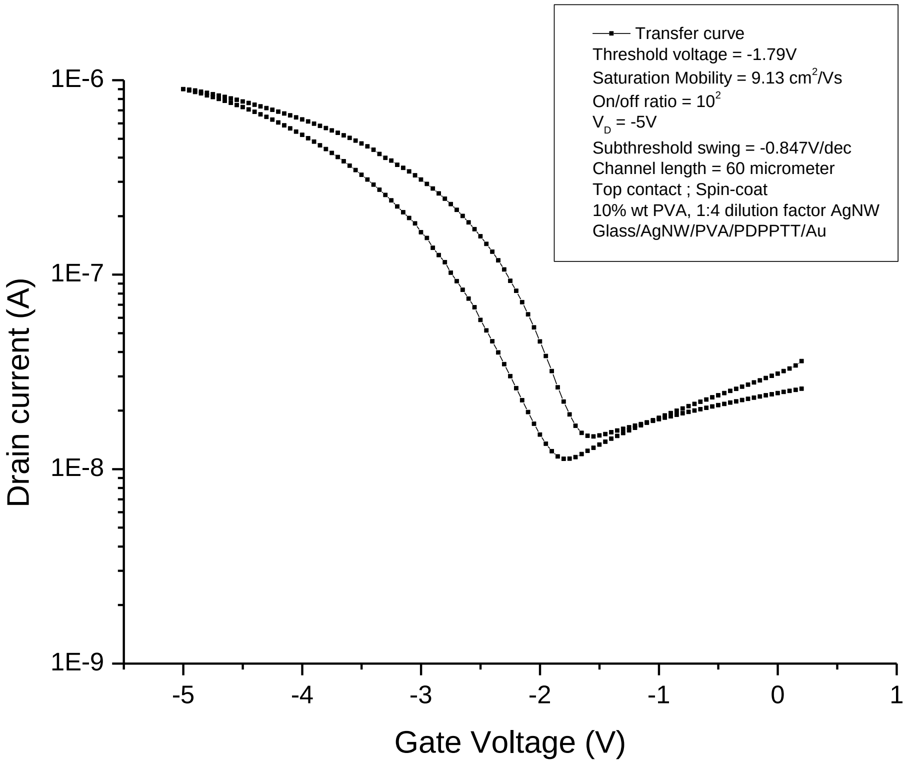


Figure 4.1.7. Typical transfer curve for Glass/AgNW/PVA/PDPPTT/Au structured OFETs.

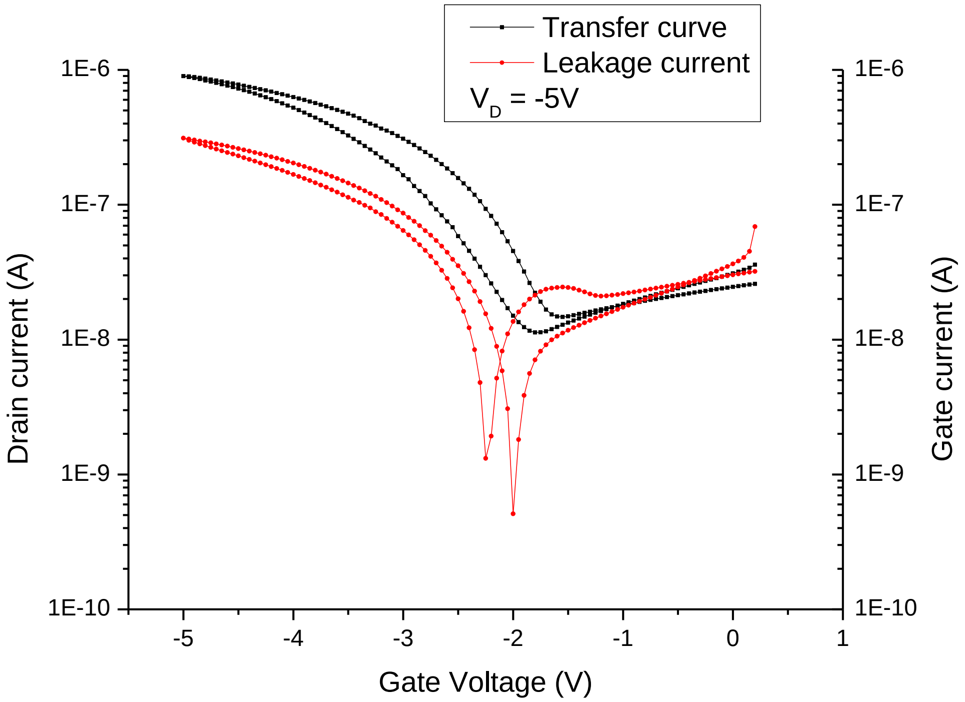


Figure 4.1.8. Transfer curve from Figure 4.1.7 showing the leakage current (red).

4.1.9. Results and Discussion

Capacitance vs. Frequency (C-f) characterization of Metal-Insulator-Metal (MIM) capacitors was done for evaluating the gate dielectric capacitance. The capacitor measurements were taken using a 3-point probe set up. Capacitor was fabricated using AgNW/PVA/AgNW (MIM) structure and capacitance per unit area was measured at 10 kHz. A capacitance value per unit area of 1.205 x 10^{-9}F/cm^2 was obtained.

Organic Field Effect Transistor (OFET) devices were fabricated using silver nanowires (AgNWs) as the gate electrode and Polyvinyl Alcohol (PVA) as the high-K dielectric to be used as gate insulating material to fabricate low-voltage PDPPTT field-effect transistors (FETs). Poly Vinyl Alcohol is well well-matched as an inexpensive, non-toxic, commercially accessible polymer with two important properties: it is soluble in water, insoluble in organic solvents and it has a relatively high dielectric constant (k = 7.8) reliant on the film thickness in the range of a hundred nanometres to many micrometres. Polyvinyl Alcohol (PVA) and its copolymers can also be chemically or thermally cross-linked at their hydroxyl groups, which produces water as a by-product. Highly cross-linked Polyvinyl Alcohol (PVA) does not tend to absorb moisture from the air and inhibits ion movement in the film, thereby decreasing leakage currents.

There was a huge leakage through the dielectric and few devices were operational. This could be attributed to the poor patterning of the device. Therefore, to minimize these undesirable effects associated with semiconductors, active layers in Organic Field Effect Transistors must be patterned and reasonably thin. Besides, aligning and patterning the semiconductors would also disable crosstalk between transistors in integrated circuits and improve overall performance of the devices. In the ideal case, semiconductors should be deposited only in the channel area.

Unfortunately, Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene (PDPPTT) in the devices made on unmodified Polyvinyl Alcohol (PVA) was not the subject of patterning, and although the insulator alone displayed relatively low leakage currents, in these devices the leakage currents can be obviously observed.

A charge carrier mobility of 9.13cm^2/V. s, threshold voltage of -1.79V and on/off ratio of 10^2 was obtained. Leakage is high, threshold voltage is low, Subthreshold swing is -0.847V/dec which is also lower but low voltage operation (-5V) has also been achieved with this organic dielectric, Polyvinyl Alcohol (PVA). The mobility achieved with the silver nanowires as electrodes is high and this result is very encouraging.

It is a good step forward taking into consideration that most of the Organic Field Effect Transistor (OFET) fabrication process is solution processed, carried out near room temperature and is scalable, except for the top contact electrodes (Evaporated Gold, Au) thus providing an attractive pathway for future large-area plastic electronics. This performance is expected to improve further by patterning the Polyvinyl Alcohol (PVA) slightly to reduce the leakage current or by reducing the thickness of the Polyvinyl Alcohol (PVA) and by using a higher k dielectric/Self Assembled Monolayer (SAM) for increased capacitance and by patterning the gate electrodes.

Solution processed source and drain electrodes using an ink jet printer to pattern source and drain contacts using silver nanoparticles for the development of a fully solution processed Organic Thin Film Transistor (OTFT) need to be investigated in the future. Modification of bottom contact structures with 2,3,4,5,6-pentafluorothiophenol (PFBT) to improve work functions of the metal can also be carried out in the future. Further optimization required will be discussed in the next chapter which involves reducing the thickness of the Poly Vinyl Alcohol (PVA) (Increasing the capacitance).

The table 4.1 below shows the summarized device characteristics of Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene)PDPPTT-based Organic Field Effect Transistors (OFETs) with different dielectrics using Silicon/Aluminium/AgNWs respectively as gate electrodes.

Table 4.1. Device characteristics of PDPPTT based OFETs with different dielectrics using Silicon/Aluminium/AgNWs, respectively, as gate electrodes.

Insulator (Gate dielectric)	Capacitance (nF/cm^2)	Dielectric constant (K)	Mobility (μ_{sat}) cm^2/V. s	Threshold voltage (V_T)	Subthreshold swing (SS) (V/Dec)	On/off ratio	Operational voltage (V_D)
SiO_2	4.69	3.9	1.33 x 10^{-1}	-7.258	-9.158	10^4	-40V
Al_2O_3	60	9.9	1.49 x 10^{-1}	0.29	0.159	10^3	-1.5V
PVA	1.205	7.8	9.13	-1.79	-0.847	10^2	-5V

4.2. Optimization of dielectric by reducing thickness to increase capacitance and reduce leakage current on low voltage OFETs by increasing the thickness

Organic Field Effect Transistor (OFET) devices with different thickness of the dielectric (Polyvinyl Alcohol (PVA) i.e., different weight by volume ratios (1% -11%) for channel lengths 20-100 µm (micrometre) and width 2000 micron were fabricated using Aluminium as the gate electrode to reduce the leakage current through the device. Prior to characterization, to further reduce leakage current, the semiconductor layer was patterned by scratching the film using a wooden toothpick to segregate adjacent transistors.

It can be shown from figure 4.2 that the leakage current is higher at lower concentrations of the Polyvinyl Alcohol (PVA) (1% weight to volume ratio (w.v) but reduces at higher concentrations of the Polyvinyl Alcohol (PVA) (11% weight to volume ratio (w.v). This is due to reduction in tunnelling currents at higher thicknesses of the insulator/dielectric. As shown in figure 4.2, the leakage current tends to reduce by 10% from 0.1 micro amps (µA) (blue line) at 1% (weight to volume ratio, w.v) Polyvinyl Alcohol (PVA) to about 0.01 microamps at 11% (weight to volume ratio (w.v) Poly vinyl Alcohol (PVA) (dark blue line (µA) due to the increased thickness of the dielectric film.

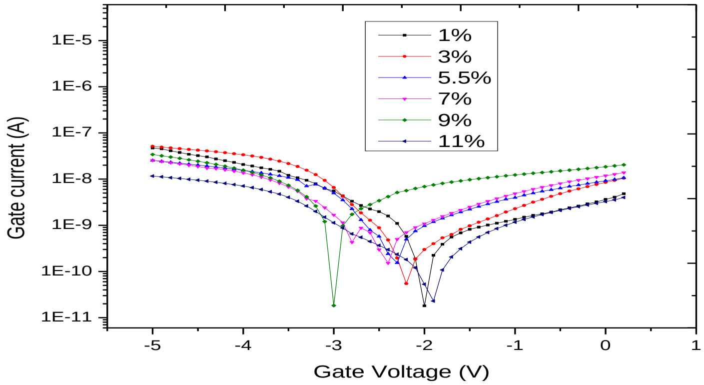


Figure 4.2. Leakage current through devices for different polyvinyl alcohol (PVA) concentrations (1-11%) (weight to volume ratios) w.v for channel length 20 micron using aluminium as the gate electrode

The transfer curve is also shown for devices with different Polyvinyl Alcohol (PVA) concentrations (1-11%) weight to volume ratio (w.v).

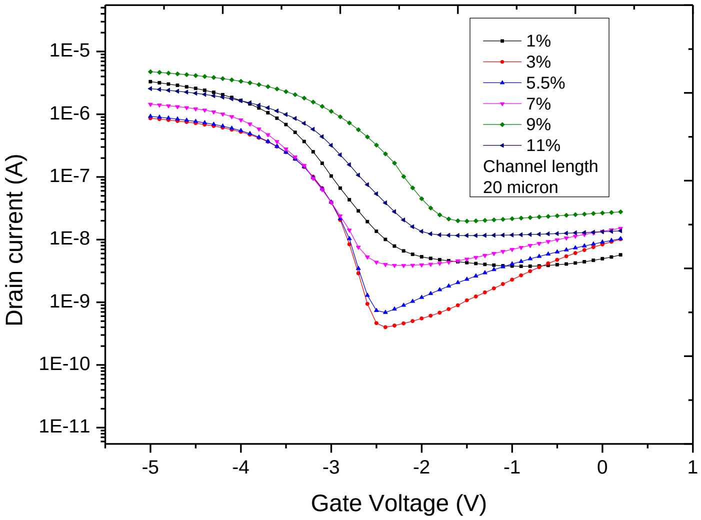


Figure 4.2.1. Transfer curves for OFETs using different Polyvinyl Alcohol (PVA) concentrations (1-11%) (weight to volume ratios) (w.v) for channel length 20 micron using aluminium as the gate electrode.

After the leakage current had been investigated to an acceptable degree, new Organic Field Effect Transistor (OFET) devices were fabricated using the higher concentration of the dielectric (11% w.v) because using this concentration gives better results due to the film forming abilities on the semiconductor and their device characteristics were analysed in the next sub-chapter.

4.2.1. Device performance of low voltage OFETs using aluminium as gate electrode

27 Organic Field Effect Transistor (OFET) devices (Device batch 1-3) 9 devices using Aluminium as gate electrode, Poly vinyl Alcohol (PVA) as dielectric at 11% (weight to volume ratio) w.v, Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) as semiconductor, and Gold as top contact electrode on each glass slide (channel length 20-100 µm and channel width 2000 micron for all the devices)) were fabricated and the data were plotted in the form of graphs for comparison purposes. The 27 devices were fabricated using the same procedure on the same day to confirm that we can get reproducible and consistent results with this transistor devices.

4.2.2. Experimental details

Substrate Preparation: Glass slides were used as a substrate and cut into 1cm-by-1cm size. The glass slides were thoroughly cleaned with acetone and methanol in a bath using the sonicator and immediately dried with a nitrogen gun.

Aluminium (Al) was thermally evaporated on the glass substrate as gate electrode at thickness of about 250nm.

Dielectric/insulator preparation: Poly (vinyl alcohol) (PVA) was purchased from Sigma Aldrich, (M_w = 89,000 – 98,000 99+% hydrolysed). A 11 w.t% solution of high molecular Polyvinyl Alcohol (PVA) was prepared by measuring out 0.33g and adding this slowly to a beaker containing 3ml of water, with stirring. The mixture was heated at 100 degrees centigrade, stirring occasionally until the solution was clear to avoid boiling the solution.

Metal and Semiconductor preparation: The Polyvinyl Alcohol (PVA) solution was spin cast onto the Glass/Aluminium (Al) sample at 1500rpm for 15 seconds and heated at 100ºC for 1 hour. Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) was spin cast onto the glass/Al/PVA structured sample and annealed under nitrogen at 120ºC for 30 minutes. Gold was evaporated through a shadow mask onto the sample as a top contact to form source and drain electrodes. The figure below shows the Glass/Al/PVA/PBDDTT/Au Organic Field Effect Transistor (OFET) structure.

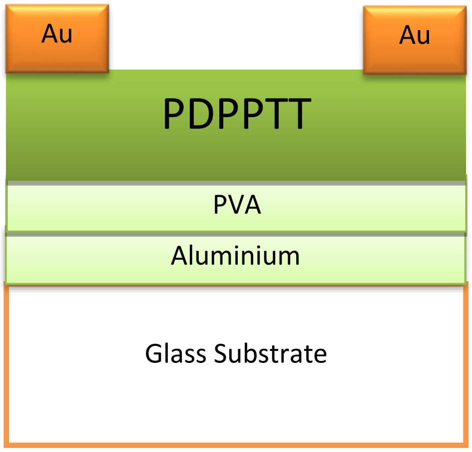


Figure 4.2.2. A schematic of the device structure when using AgNWs as gate electrode/PVA as dielectric.

4.2.3. Results and discussion

Based on the figures and data in the table below (Figure 4.2.3a, b, c, d, figure 4.2.3.1), and (table 4.2, 4.3 and 4.4) it can be shown that most of the devices are operational with similar characteristics.

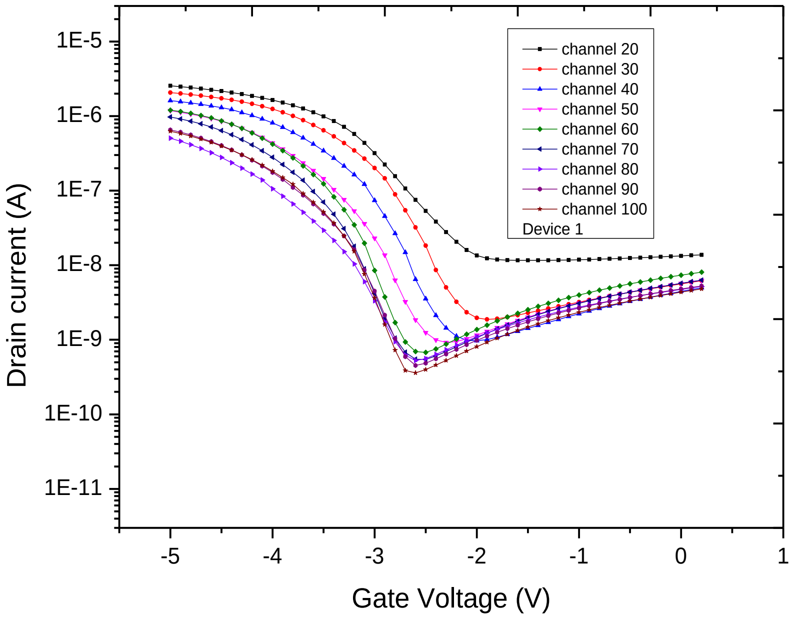
The Organic Field Effect Transistors (OFETs) have field-effect mobility ranging from 8 to 20cm^2/V.s, an on/off current ratio of 10^3, a subthreshold swing ranges from 270mV/decade to 470mV/decade, a threshold voltage of -1.5V to -3.00V and minimal hysteresis as shown in figure 4.2.3.1. The threshold voltage is high for this device that operates at -5V. This may indicate that there a lot of traps in dielectric hence a surface treatment of the PVA may be required to smoothen out the film.

To remove interfacial dipoles and trap states, we may introduce a Self-Assembled Monolayer at the interface between the Polyvinyl Alcohol (PVA) and the semiconductor Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene)(PDPPTT) leading to the desirable characteristics we want.

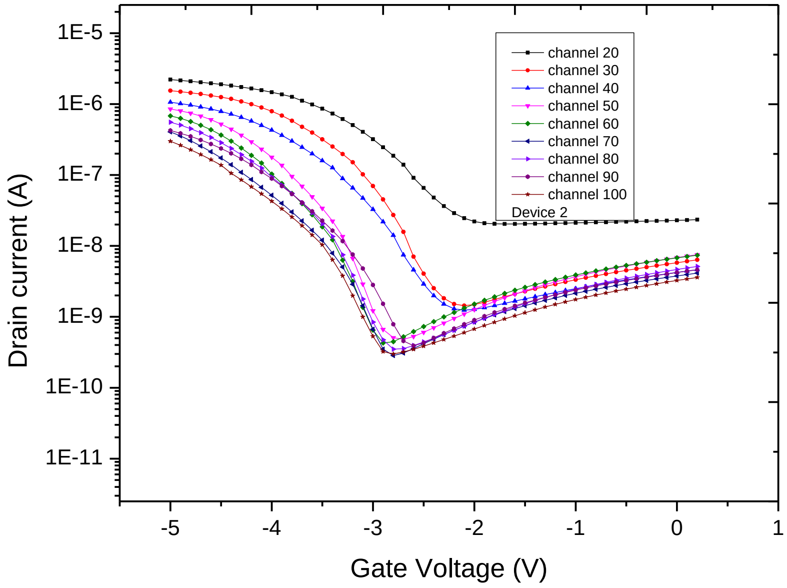
The use of a self-assembled monolayer (octadecyl trichlorosilane (ODTS)) may reduce the traps in the dielectric therefore reducing the hysteresis a bit further and reduce the threshold voltage. There is also an increasing trend of the charge carrier mobility with an increase in channel length for the device.

Transfer curves of the low voltage OFETs using Aluminium as gate electrode:

(a) Device batch 1: Yield 100%



(b) Device batch 2: Yield 100%



(c) Device batch 3: Yield 88.8%

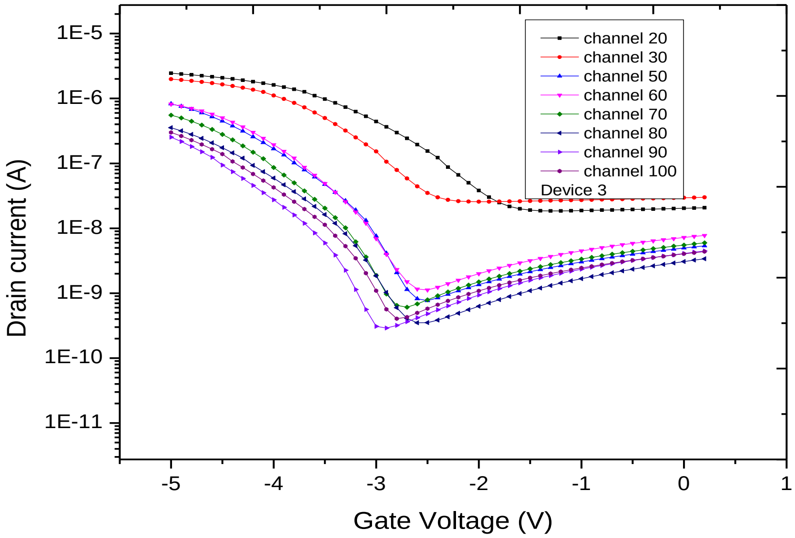
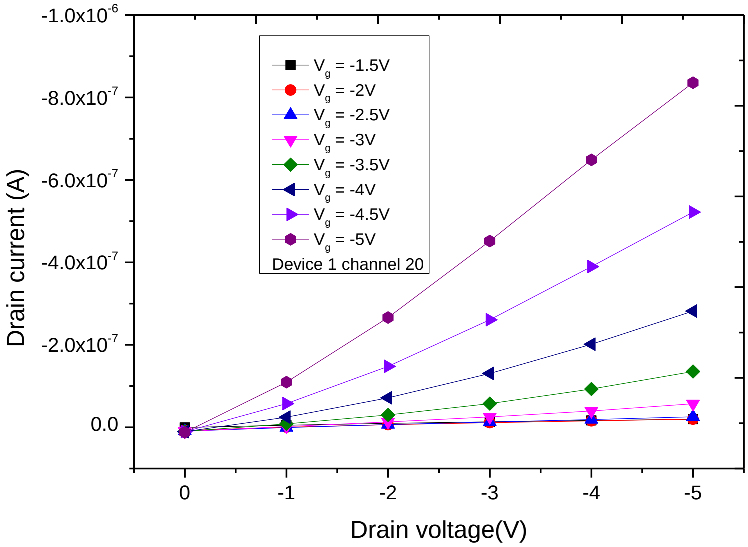


Figure 4.2.3. Transfer curves for device batch 1, 2 and 3 at various channel lengths (i.e., 20 -100micron)



(a) Output characteristics of the OFET device at 11% PVA at 20 microns.

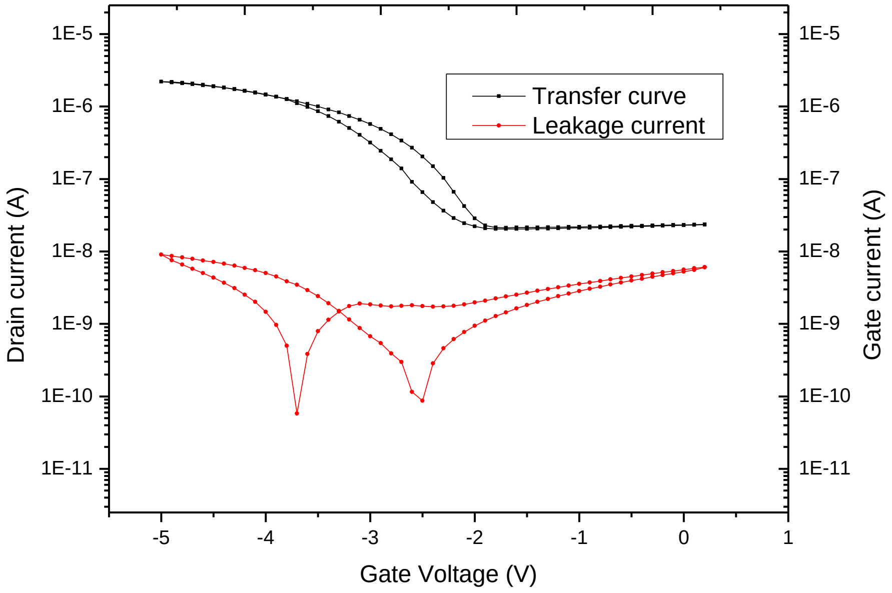


Figure 4.2.3.1. OFET Device using aluminium as gate electrode showing hysteresis at channel length 20 micron.

The table below shows the Organic Field Effect Transistor (OFET) performance characteristics of same device configurations and dimensions with semiconductor (PDPPTT) at variable channel lengths 20-100 microns as measured under ambient conditions.

Experimental Data for transistor devices using aluminium as the contact electrodes (gate).

Table 4.2: Device 1 (Device Yield = 100% of the devices were operational)

Channel length (L) (micron)	Threshold voltage (Forward sweep) (V_T)	Saturation Mobility (Forward sweep) (μ) $cm^2/V. s$	On/off ratio	Subthreshold swing (V/dec)
20	-2.10	12.8	10^3	0.38
30	-2.25	14.6	10^3	0.35
40	-2.44	14.7	10^3	0.26
50	-2.58	14.9	10^3	0.19
60	-2.76	19.1	10^3	0.25
70	-2.85	19.6	10^3	0.29
80	-2.77	12.70	10^3	0.28
90	-2.76	15.4	10^3	0.17
100	-2.76	15.4	10^3	0.17

Table 4.3: Device 2 – (Device Yield 100% of the devices were operational)

Channel length (L) (micron)	Threshold voltage (Forward sweep) (V_T)	Saturation Mobility (Forward sweep) (μ) $cm^2/V. s$	On/off ratio	Subthreshold swing (Forward sweep) (V/dec)
20	-2.15	10.2	10^3	0.47
30	-2.42	11.8	10^3	0.47
40	-2.45	11.10	10^3	0.47
50	-2.99	13.7	10^3	0.37
60	-3.00	17.5	10^3	0.22
70	-2.91	13.6	10^3	0.29
80	-2.94	14.5	10^3	0.21
90	-2.75	12.7	10^3	0.29
100	-2.95	13.6	10^3	0.25

Table 4.4: Device 3 – (Device Yield 89% of the devices were operational)

Channel length (L) (micron)	Threshold voltage (Forward sweep) (V_T)	Saturation Mobility (Forward sweep) (μ) $cm^2/V. s$	On/off ratio	Subthreshold swing (Forward sweep) (V/dec)
20	-1.80	8.47	10^3	0.35
30	-2.43	11.2	10^3	0.47
50	-2.73	13.1	10^3	0.22
60	-2.82	16.2	10^3	0.25
70	-2.90	15.5	10^3	0.31
80	-2.79	11.0	10^3	0.30
90	-3.00	12.9	10^3	0.34
100	-2.85	13.8	10^3	0.27

In total, the 27 Organic Field effect Transistor (OFET) devices measured showed a mobility range from 8cm^2/V. s to 20cm^2/V.s. The figure 4.2.3.2 below shows the mobility distribution for the 27 Organic Field Effect Transistor (OFET) devices measured using the same device configurations and dimensions with the same semiconductor solution-Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) and Polyvinyl Alcohol (PVA) dielectric solution at 11% (weight to volume (w.v) at variable channel lengths 20-100 micron as measured under ambient conditions.

As shown, 23% of the devices showed a mobility of 15cm^2/V. s, the observed mobility was at 1-2 orders of magnitude higher than the values of about 0.17cm^2/V. s obtained when using a thinner dielectric film at 1% (weight to volume) w.v Polyvinyl Alcohol (PVA) dielectric.

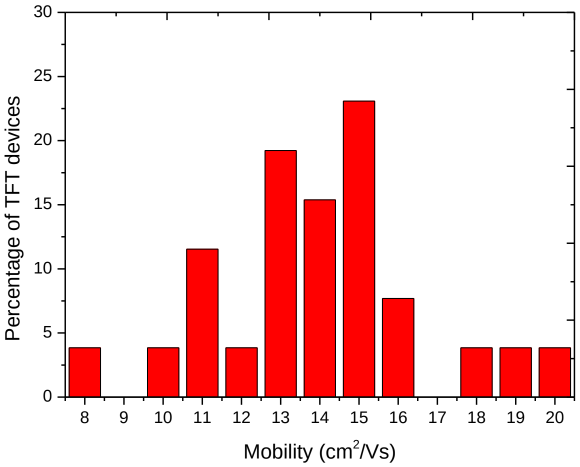


Figure 4.2.3.2. The mobility distribution for 27 devices showing mobility ranging from 8cm^2/V. s to 20cm^2/V. s

4.2.4. Device performance of low voltage OFETs using pristine silver nanowires as gate electrode

Here, Pristine silver nanowire solutions were used to fabricate OFET transistor devices. Silver nanowires (AgNWs) were purchased from Seashell Technologies as supplied with a concentration of 5 mg/ml in isopropyl alcohol (IPA). The mean length of the nanowires was 19.6 micrometer (µm) with a mean diameter of 23 nanometre (nm) as provided by the supplier.

4.2.5. Experimental details

Substrate Preparation: Glass slides were used as a substrate and cut into 1cm-by-1cm size. The glass slides were thoroughly cleaned with acetone and methanol in a bath using the sonicator and immediately dried with a nitrogen gun.

Gate Electrode preparation: A drop of silver paint was deposited at one of the edges of the glass substrate and left to dry to improve the contact with the bottom silver nanowire transparent conducting electrode that is to be deposited on top of it.

The Pristine solution of silver nanowires (AgNWs) was spin cast at 1500rpm for 40 seconds to allow the solvent to evaporate. The sample was annealed under nitrogen at a temperature of 140 degrees centigrade for 5 minutes to fuse the junctions in the silver nanowires.

Dielectric preparation: Poly (vinyl alcohol) (PVA) was purchased from Sigma Aldrich, (Molecular weight, M_w = 89,000 – 98,000 99+% hydrolysed). A 11 w.t% solution of high molecular Polyvinyl Alcohol (PVA) was prepared by measuring out 0.33g and adding this slowly to a beaker containing 3ml of water, with stirring. The mixture was heated at 100 degrees centigrade, stirring occasionally until the solution was clear to avoid boiling the solution.

Metal and Semiconductor preparation: The Polyvinyl Alcohol (PVA) solution was spin cast onto the Glass/pristine silver nanowire sample at 1500rpm for 15 seconds and heated at 100ºC for 1 hour.Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) was spin cast onto the glass/silver nanowires (AgNWs)/Polyvinyl Alcohol (PVA) structured sample and annealed under nitrogen at 120ºC for 30 minutes. Gold was evaporated through a shadow mask onto the sample as a top contact to form source and drain electrodes. The figure 32 shows the Glass/AgNW/PVA/PBDDTT/Au Organic Field Effect Transistor (OFET) structure.

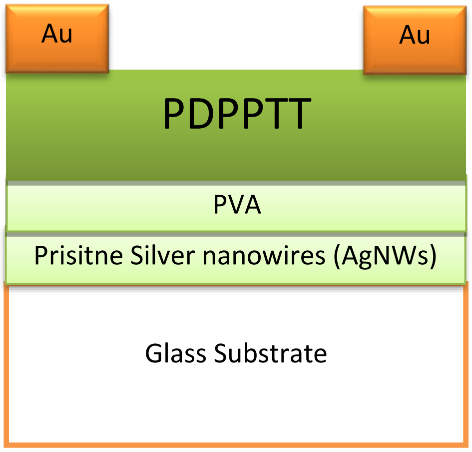


Figure 4.2.4: Showing device structure when using Pristine AgNWs as gate electrode/PVA as dielectric.

The devices were taken for measurement. The following figure 4.2.5 shows the Transfer characteristics of the organic Field Effect Transistors (OFETs).

4.2.6. Results and discussion

Based on the figures and data in the table below (Figure 4.2.5, 4.2.6, 4.2.7, 4.2.8), and (table 4.5) it can be shown that most of the devices are operational (Device Yield = 67% of the devices were operational) with similar characteristics. The Organic Field Effect Transistors (OFETs) have field-effect mobility ranging from 7.30 to 18.9cm^2/V. s, an on/off current ratio of 10^3, a subthreshold swing ranges from 0.39V/decade to 0.47V/decade, a threshold voltage of -1.7V to -1.85V and minimal hysteresis as shown in figure 4.2.8. The threshold voltage is less compared to the Organic Field Effect Transistors (OFETs) fabricated with the use of Aluminium gate electrodes. This may indicate that there are less traps in this Organic Field Effect Transistor (OFET) device.

Transfer curves of the low voltage OFETs using Pristine AgNWs as gate electrode

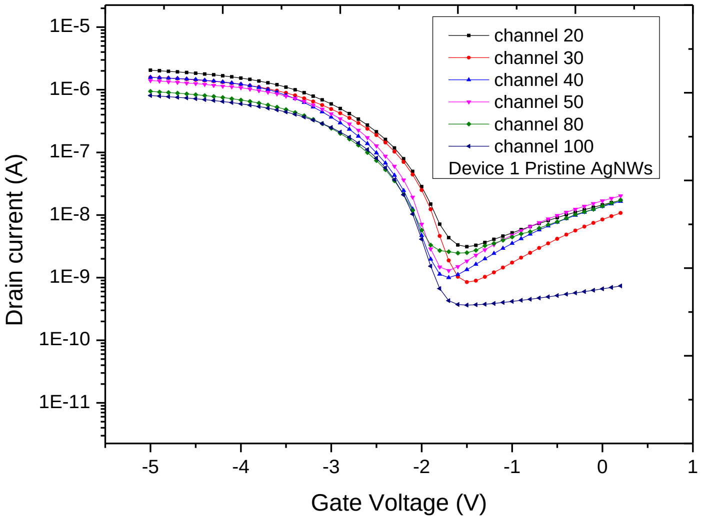


Figure 4.2.5. Transfer characteristics (I_d versus V_g) at V_d = -5V of the PDPPTT Film OFET at channel lengths 20-100 microns with pristine silver nanowire gate electrode.

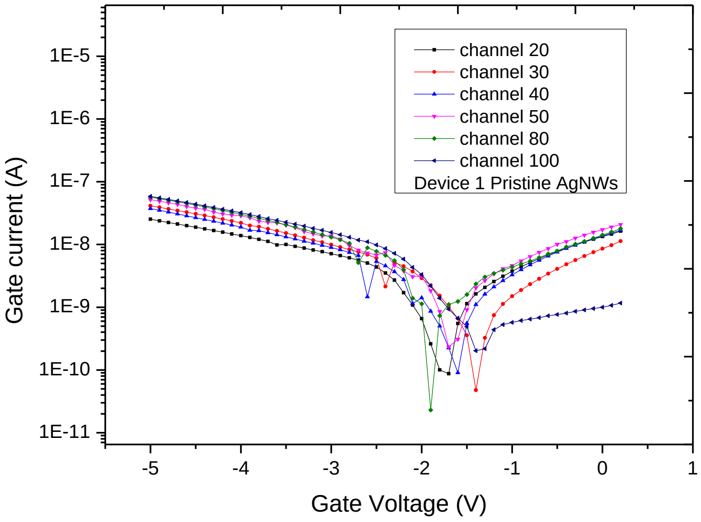


Figure 4.2.6. Leakage current through PVA dielectric of the PDPPTT Film OFET at channel lengths 20-100 microns with pristine silver nanowire gate electrode. Channel width = 2000micron.

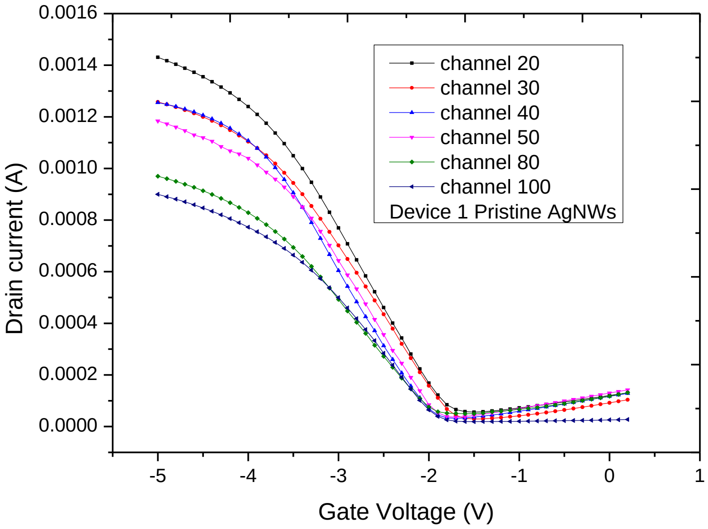


Figure 4.2.7. Sqrt I_d versus V_g of the PDPPTT Film OFET at channel lengths 20 micron with pristine silver nanowire gate electrode. Channel width = 2000micron.

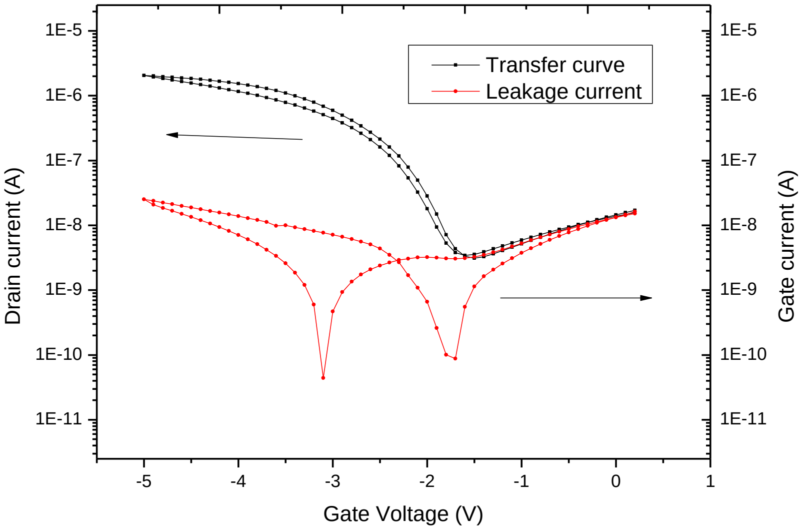


Figure 4.2.8. Transfer characteristics showing hysteresis of the PDPPTT Film OFET at channel lengths 20-100 microns with pristine silver nanowire gate electrode and leakage current through the PVA dielectric.

Table 4.5: Measured Parameters for PDPPTT organic field effect transistors at channel lengths 20-100 microns with pristine silver nanowire gate electrode. (Device Yield = 67% of the devices were operational).

Channel Length (L) (micron)	Threshold (V_T)	Mobility (µ) $cm^2/V.s$)	On/off ratio	Subthreshold swing (V/dec)
20	-1.70	7.30	10^3	0.39
30	-1.70	8.45	10^3	0.44
40	-1.84	14.40	10^3	0.47
50	-1.84	16.10	10^3	0.39
80	-1.94	15.00	10^3	0.43
100	-1.85	18.9	10^3	0.45

4.2.7. Device Performance of low voltage OFETs using Optimized Silver nanowires as gate electrode

Here, Optimized silver nanowire solutions were used to fabricate Organic Field Effect Transistor devices. Silver nanowires (AgNWs) were purchased from Seashell Technologies as supplied with a concentration of 5 mg/ml in isopropyl alcohol (IPA). The mean length of the nanowires was 19.6 micrometer (µm) with a mean diameter of 23 nanometre (nm) as provided by the supplier.

4.2.8. Experimental details

Substrate Preparation: Glass slides were used as a substrate and cut into 1cm-by-1cm size. The glass slides were thoroughly cleaned with acetone and methanol in a bath using the sonicator and immediately dried with a nitrogen gun.

Gate Electrode preparation: A drop of silver paint was deposited at one of the edges of the glass substrate and left to dry to improve the contact with the bottom silver nanowire transparent conducting electrode that is to be deposited on top of it. Silver Nanowires in isopropanol (IPA) (silver nanowires (AgNWs0 -25), Length 15-30um, Diameter 15-35nm, 5mg/ml concentration purchased from seashell were diluted with isopropanol (IPA) by a factor of 1:4. 400µl of IPA was mixed with 100µl of silver nanowires (AgNWs) in a vial bottle.

The mixture was shaken thoroughly until a homogenous mixture was obtained. The solution was spin cast at 1500rpm for 40 seconds to allow the solvent to evaporate. The sample was annealed under nitrogen at a temperature of 140 degrees centigrade for 5 minutes to fuse the junctions in the silver nanowires

Dielectric preparation: Poly (vinyl alcohol) (PVA) was purchased from Sigma Aldrich, (M_w = 89,000 – 98,000 99+% hydrolysed). A 11 w.t% solution of high molecular Polyvinyl Alcohol (PVA) was prepared by measuring out 0.33g and adding this slowly to a beaker containing 3ml of water, with stirring. The mixture was heated at 100 degrees centigrade, stirring occasionally until the solution was clear to avoid boiling the solution.

Metal and Semiconductor preparation: The Polyvinyl Alcohol (PVA) solution was spin cast onto the Glass/silver nanowire sample at 1500rpm for 15 seconds and heated at 100ºC for 1 hour. Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene (PDPPTT)was spin cast onto the glass/AgNWs/PVA structured sample and annealed under nitrogen at 120ºC for 30 minutes. Gold was evaporated through a shadow mask onto the sample as a top contact to form source and drain electrodes. The figure below shows the Glass/AgNW/PVA/PBDDTT/Au OFET structure.

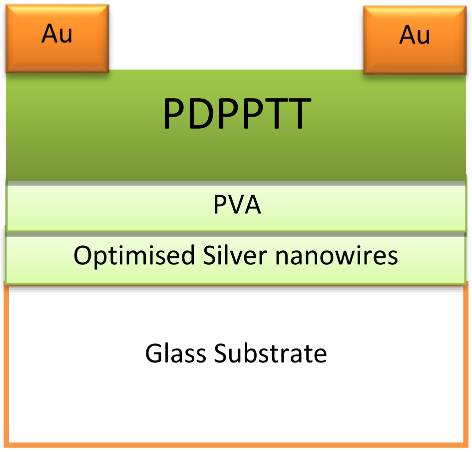


Figure 4.2.9. Device structure when using optimised AgNWs as gate electrode/PVA as dielectric.

4.2.9. Results and discussion

Based on the figures and data in the table below (Figure 38, 39, 40, 41), and (table 5) it can be shown that most of the devices are operational (Device Yield = 89% of the devices were operational) with similar characteristics. The Organic Field Effect Transistors (OFETs) have field-effect mobility ranging from 2.23 to 19.5cm^2/V. s, an on/off current ratio of 10^3, a subthreshold swing ranges from 0.26V/decade to 0.58V/decade, a threshold voltage of -0.68V to -1.77V and minimal hysteresis as shown in figure 4.2.9.4. The threshold voltage is less compared to the Organic Field Effect Transistors (OFETs) fabricated with the use of Aluminium and Pristine gate electrodes. This may indicate that there are less traps in this Organic Field Effect Transistor (OFET) device.

Transfer curves of the low voltage OFETs using Optimized AgNWs as gate electrode

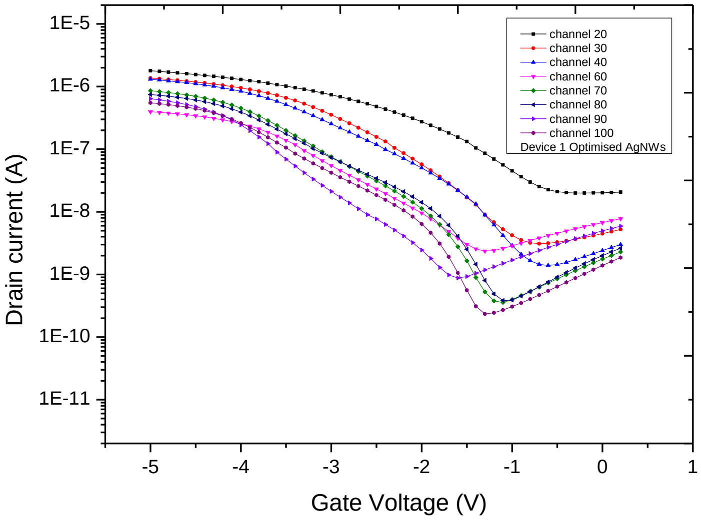


Figure 4.2.9.1. Transfer characteristics (I_d versus V_g) at V_d = -5V of the PDPPTT Film OFET at channel lengths 20-100 microns with optimized AgNW gate electrode.

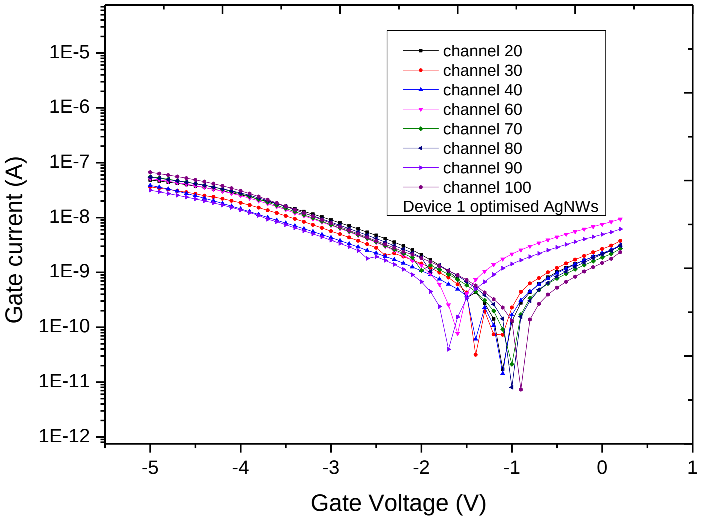


Figure 4.2.9.2. Leakage current through PVA dielectric of the PDPPTT Film OFET at channel lengths 20-100 microns with optimized silver nanowire gate electrode. Channel width = 2000micron.

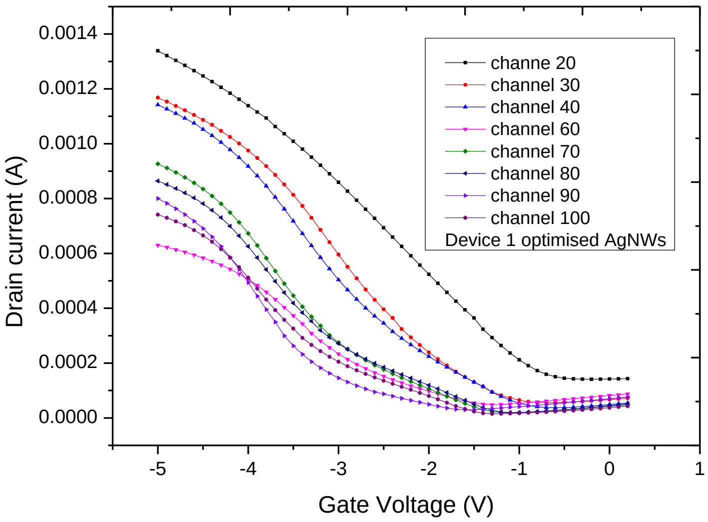


Figure 4.2.9.3. Sqrt I_d versus V_g of the PDPPTT Film OFET at channel lengths 20-100 microns with optimized silver nanowire gate electrode. Channel width = 2000micron.

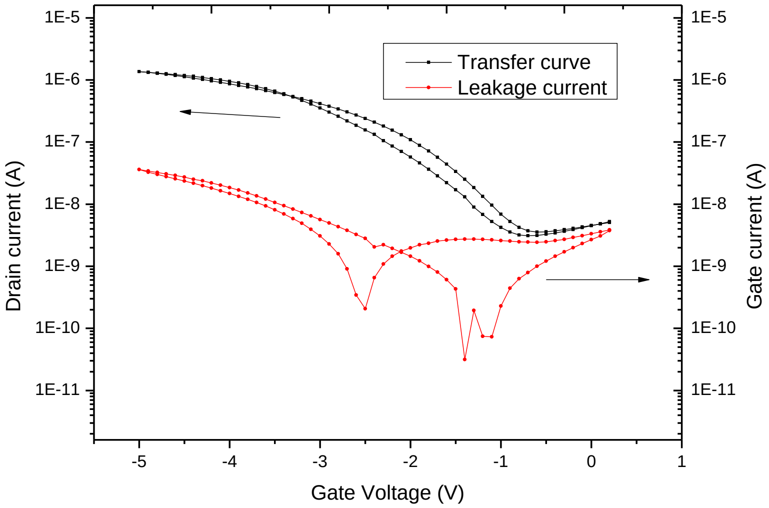


Figure 4.2.9.4. Transfer characteristics showing hysteresis of the PDPPTT Film OFETs at channel lengths 30 micron with optimized silver nanowire gate electrode and leakage current through the PVA dielectric.

Table 4.6: Measured Parameters for PDPPTT organic field effect transistors at channel lengths 20-100 microns with optimized silver nanowire gate electrode (Device Yield = 89% of the devices were operational).

Channel Length (L) (micron)	Threshold (V_T)	Mobility (μ_{sat}) $cm^2/V. s$)	On/off ratio	Subthreshold swing (V/Dec)
20	-0.68	2.23	10^2	0.37
30	-1.07	5.12	10^3	0.39
40	-1.07	7.07	10^3	0.26
60	-1.39	4.71	10^2	0.58
70	-1.40	12.4	10^3	0.27
80	-1.23	11.5	10^3	0.39
90	-1.77	19.5	10^3	0.37
100	-1.47	13.8	10^3	0.34

4.3. Device Performance of low voltage OFETs using Indium Tin Oxide (ITO) as gate electrode

Here, Indium Tin Oxide coated glass substrates were used to fabricate Organic Field Effect Transistor (OFET) devices. Organic Field Effect Transistor (OFET) devices gated by Polyvinyl Alcohol with high capacitance materials enable lower operating voltages, reduced power consumption and improved performance. Several strategies have been developed, including reducing dielectric thickness and using high-k dielectrics, to achieve large capacitances but here we use a different gate electrode (Indium Tin Oxide) to fabricate organic field effect transistors that exhibit smaller threshold voltages. Indium Tin Oxide (ITO) is a popular transparent conducting oxide which has been used as high work function electrode in organic field effect transistors. Indium Tin Oxide films show excellent transmission characteristics in the visible and infrared spectrum while maintaining high electrical conductivity. High work function electrodes are used to inject holes into organic materials. In majority applications the Indium Tin Oxide work function has an impact on the device performance as it affects the energy barrier height at the interface. Hence, the work function of Indium Tin Oxide is of vital importance.

4.3.1. Experimental details

Substrate/Gate electrode Preparation: Indium Tin Oxide coated glass substrates was prepared for the utilization in Organic Field Effect Transistors (OFETs).

Dielectric preparation: Poly (vinyl alcohol) (PVA) was purchased from Sigma Aldrich, (Molecular weight, M_w = 89,000 – 98,000 99+% hydrolysed). A 11 w.v% (weight to volume ratio) solution of high molecular Polyvinyl Alcohol (PVA) was prepared by measuring out 0.33g and adding this slowly to a beaker containing 3ml of water, with stirring. The mixture was heated at 100 degrees centigrade, stirring occasionally until the solution was clear to avoid boiling the solution.

Metal and Semiconductor preparation: The PVA solution was spin cast onto the Glass/Indium Tin Oxide (ITO) sample at 1500rpm for 15 seconds and heated at 100ºC for 1 hour. Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) was spin cast onto the glass/Indium Tin Oxide (ITO)/Polyvinyl Alcohol (PVA) structured sample and annealed under nitrogen at 120ºC for 30 minutes. Gold was evaporated through a shadow mask onto the sample as a top contact to form source and drain electrodes. The figure below shows the Glass/ITO/PVA/PBDDTT/Au Organic Field Effect Transistor (OFET) structure.

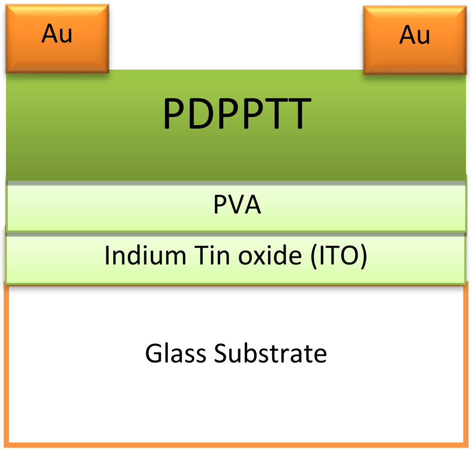


Figure 4.3.1. Device structure when using ITO as gate electrode/PVA as dielectric.

4.3.2. Results and discussion

Based on the figures and data in the table below (Figure 4.3.2 and 4.3.3), it can be shown that the Organic Field Effect Transistors (OFETs) have field-effect mobility of 14.6cm^2/V. s, an on/off current ratio of 10^4, a subthreshold swing of 0.43V/decade, a threshold voltage of -1.86V and some hysteresis as shown in figure 31.

Table 4.7 shows a comparison of Organic Field Effect Transistor (OFET) performance when using different gate electrodes.

Generally, to adjust the gate threshold voltage, fixed charges or traps need to be minimized in the gate dielectric, at the dielectric interface. Subthreshold Swing (SS) describes how fast the channel could switch on and off; hence, Subthreshold Swing (SS) should be minimized for fast switching. A smaller Subthreshold swing (SS) shrinks gate voltage (V_G) spanning required to fully turn the channel on and off (i.e., lower threshold and operating (supply) voltages).

Interface states (large numbers of traps and defects) increase the subthreshold swing (SS). To reduce the SS, High k dielectric can be used, or the Organic Semiconductor/dielectric interface can be treated with a Self-Assembled Monolayer (SAM) or polymer.

Since the threshold voltage determines the requirements for turning the Organic Field Effect Transistors (OFET) transistor on or off, it is important to be able to adjust threshold voltage in designing the device. In this report, we report on a reduction of threshold voltage (V_T) in Polyvinyl Alcohol (PVA) Organic Field Effect Transistors (OFETs) by changing the metal of the gate from an Evaporated Aluminium through a highly expensive vacuum procedure to a low-cost spin coating deposition of metal silver nanowires as the gate electrode in an Organic Field Effect Transistor (OFET).

Transfer curves of the low voltage OFETs using ITO as gate electrode

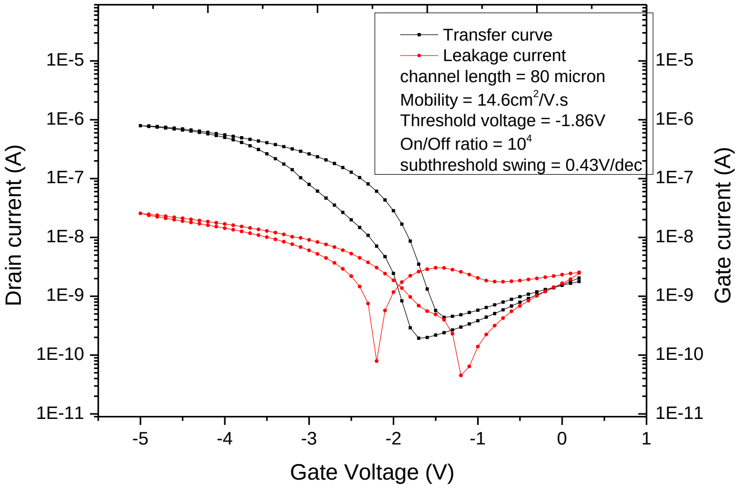


Figure 4.3.2. Transfer characteristics and leakage current of PDPPTT organic field effect transistors at channel lengths 80 microns with ITO coated gate electrode.

The work function potential difference is determined by choice of the gate conductor material. Since threshold voltage (V_T) depends on the choice of the gate electrode material (i.e., the gate electrode work function) has an impact on the threshold voltage. Silver nanowire (AgNW) has a work function of 4.0eV and Aluminium has a work function of 4.28eV and Indium Tin Oxide (ITO) has a work function of 4.8eV. A low work function gate electrode such as (silver nanowires and indium tin oxide) reduces the threshold voltage as shown in the device characteristics; the silver nanowires optimized devices exhibit smaller threshold voltages, as well.

From the PDPPTT Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) Organic Field Effect Transistor (OFET) devices using Indium Tin Oxide electrode as gate, we have higher ON/OFF ratio of 10^4, this is one order of magnitude higher than the OFET devices using silver nanowires (AgNWs) electrode as gate electrode.

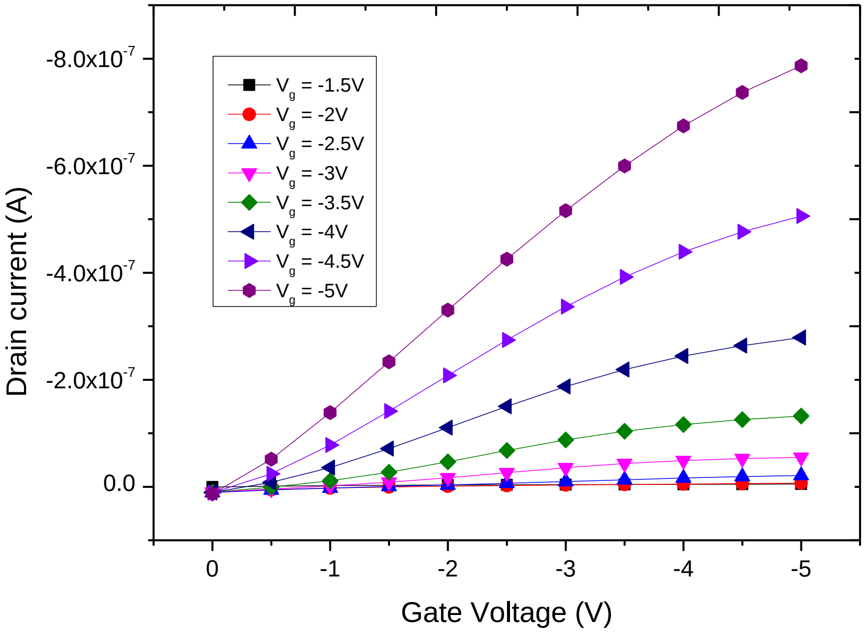


Figure 4.3.3: Output characteristic using ITO at channel length 100microns.

Table 4.7: comparison of OFET performance when using different gate electrodes.

Gate Electrode	Threshold voltage (V_T)	Mobility (μ_{sat}) $cm^2/V.\ s$)	On/off ratio	Subthreshold swing (V/Dec)
Aluminium	-2.77V	12.70	10^3	0.28
ITO	-1.86V	14.6	10^4	0.43
Pristine Silver nanowires	-1.94	15.0	10^3	0.43
Optimized Silver nanowires	-1.23	11.5	10^3	0.39

Chapter 5

Conclusions

The use of solution processable materials for Organic Field Effect Transistors (OFETs) onto substrates through a low-cost fabrication process may be desirable for manufacturing on large-area, flexible/rollable electronics. Printing fully solution-processed organic electronic devices may potentially revolutionize production of flexible electronics for various applications. However, difficulties in forming thin, flat, uniform films through printing techniques have been responsible for poor device performance and low yields. In this work, the problem of high operational voltages and poor electrical conductivity was solved. The operation voltage of Organic Field Effect Transistors (OFETs) has been reduced via the use of a high k dielectrics however it may be reduced further by using a Self-Assembled Monolayer (SAM) in between the semiconductor and the dielectric to improve the surface properties by removing the traps. Solution-processed silver nanowire (AgNW) electrodes to be used as transparent contacts for thin film transistors have been developed by demonstrating low sheet resistance and high transmittance. In summary, a high-K dielectric known as Polyvinyl Alcohol (PVA) is used as gate insulating material to fabricate low-voltage Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c] pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) field-effect transistors (FETs). The increased thickness of the gate insulator exhibits the excellent properties such as lower leakage current density, low surface roughness, and high dielectric constant. When operated under a low voltage of −5 V, the Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene)PDPPTT Organic Field Effect Transistor (OFET) devices fabricated with a Polyvinyl Alcohol (PVA) dielectric show the attractive electrical performance, e.g. carrier mobility (μ) of 11.5 cm^2/V.s, threshold voltage (V_T) of −1.23 V, on/off current ratio of 10^3, and subthreshold swing (SS) of 0.39V dec^{-1}, which is much better than that of devices obtained on conventional 300 nm SiO_2 substrate (1.33 X 10^{-1} cm^2 /V.s - for mobility (μ)), threshold voltage (V_T) of −7.258 V and subthreshold swing (SS) of 9.158 V dec^{-1} which is operated at −40 V. These results indicate that this kind of high-K dielectric becomes a promising candidate as gate insulator for low-voltage organic Field Effect Transistors (OFETs).

Chapter 6

Future Work

Further threshold voltage reduction using Self Assembled Monolayer (SAM) sandwiched in between the Polyvinyl Alcohol (PVA) dielectric and the Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (PDPPTT) semiconductor to improve surface properties by properly aligning the surface molecules to remove traps.

Cross link the Polyvinyl Alcohol (PVA) dielectric to increase chains of monomers hence tightly packing the molecular structures to decrease traps.

Fabrication of (PDPPTT) Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) Organic Field Effect Transistor (OFETs) using different dielectrics particularly Polyelectrolytic dielectrics for wider range of performance.

Measure contact resistance in the gate electrodes used.

Develop silver nanowire solutions for use in Printing top contact electrodes.

Develop an understanding of the developed film via the use Atomic Force Microscopy to understand the behaviour of the casted materials for optimization purposes (Characterization of materials)

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