

FABRICATION AND CHARACTERISATION OF ORGANIC THIN-FILM TRANSISTORS FOR SENSING APPLICATIONS

By

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List of Publications

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- X. Zhou, K. Mutkins, D. Elkington, K. Sirois, W. Belcher, P.C. Dastoor *Effects of Device Architecture on the Performance of Organic Thin Film Transistors.* 2008 MRS Fall Meeting
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Abstract

Organic thin-film transistors (OTFTs) are a family of devices in the area of organic electronics which are generating a large amount of interest due to the wide variety of potential applications for transistors which have all the benefits associated with using organic materials. These benefits include low-temperature and low-power fabrication possibilities, the use of flexible substrates and the low cost of materials.

Previous literature on OTFTs comprising poly-3-hexylthiophene (P3HT) semiconductor layers, poly(4-vinylphenol) (PVP) dielectric layers and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) gate electrodes have reported on their relatively high performance at low operating voltages. However, there still remains the potential for further investigations to discover more about the nature of the current modulation mechanism(s) in these types of OTFTs. Several experiments were carried out to probe their operation mechanisms and determine their suitability for applications such as biosensors. The results of many of these experiments indicated that ions donated from the acidic PEDOT:PSS gate material as well as those liberated from water in air contribute to current modulation by doping and de-doping of the P3HT semiconductor.

Poly(vinyl-pyridine) (PVPy) was then introduced as a dielectric material to replace PVP. PVPy contrasts in its chemical properties with PVP: rather than allowing and contributing to the free movement of protons within it as the acidic PVP does, the chemically basic PVPy will tend to bind protons to its pyridal groups, restricting their movement. It was shown that this change in material reduces the off current (I_{OFF}) of the devices (by inhibiting any doping of P3HT which occurs upon PEDOT:PSS deposition), however the on current (I_{ON}) was also reduced and thus no real improvement in current modulation ration (I_{ON}/I_{OFF}) was achieved.

Whilst some aspects of device performance were improved when PVPy was used as the dielectric layer instead of PVP, the current modulation ratio remained low. Subsequent experiments showed that the addition of a dopant salt (LiClO_4) to the PVPy layer can substantially increase the current modulation ratio of the OTFTs. In fact, it was demonstrated that the current modulation ratio can be controlled by varying the amount of salt added to each device. The nature of the drain current (I_D) response to changes in gate voltage (V_{GS}) in the time domain indicates that electrochemical doping, and not an electrostatic mechanism, is the nature of the mechanism causing

current modulation (similar to the previous un-doped devices). NaClO_4 was also trialled as a candidate for the dopant salt and, despite Na^+ being larger than Li^+ , it appeared to move more freely within the device which is consistent with a hydration sphere model and therefore supports the idea that the dielectric layer is moisture-rich when operating in air.

Finally, OTFTs incorporating the enzyme glucose oxidase (GOX) were fabricated for use as glucose sensors. GOX selectively oxidises glucose and it was hypothesised that the ions liberated in this oxidation reaction could contribute to the ionic processes which contribute to current modulation in the devices and therefore a relationship between the quantity of glucose exposed to the device and the I_D level could be established. The results presented here show that devices with embedded GOX do indeed show a relationship between glucose concentration and I_D when an analyte solution is deposited onto the device.

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1

Introduction

Conductive polymers are a class of organic materials which have electrical conductivity values in the semiconducting or metallic range, as opposed to possessing the insulating properties for which polymers were conventionally recognised (as in plastics) [1]. Heeger, MacDiarmid and Shirakawa received the Nobel prize for chemistry in 2000 “for the discovery and development of conductive polymers” [2]. This work, which was conducted in the 1970s, focussed on the development of doped polyacetylene [3–5]. However, the history of conductive polymers can be traced back even further to the early 1960s when Weiss et al. released a series of articles describing the synthesis and characterisation of electrically conductive polypyrrole [6, 7].

Organic electronics is a field within material sciences focussing on the fabrication and development of electronic devices which employ conductive and semiconductive organic materials. Often these are non-polymeric materials; small molecule semiconductors such as pentacene and other materials such as carbon nanotubes (hollow cylindrical carbon-based constructs) and graphene (graphite sheets of single atomic thickness) are widely used in organic electronics [8, 9]. Indeed, pentacene is considered to be one of the highest performing organic semiconductors [10]. However, conductive polymers have several advantages over other organic conductors with regards to their processability, and hence their use is becoming increasingly widespread. The organic polymeric semiconductor poly-3-hexylthiophene (P3HT) is an oft-employed and relatively well understood material [11], and it will be used as the semiconductor material in the devices presented in this thesis. Chapter 2 will include a detailed discussion on the materials used and the reasons they were chosen.

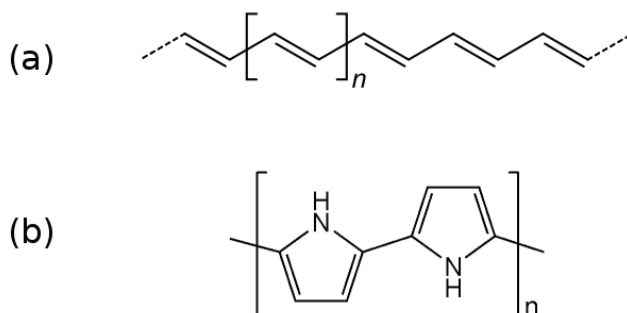


FIGURE 1.1: Early conducting polymers - (a) polyacetylene (b) polypyrrole.

There are several different categories of organic electronic devices which are currently being researched and developed, and in some cases they are already being incorporated into commercial products [12–14]. Probably the three types of devices receiving the most attention at the moment are: organic thin film transistors (OTFTs) [15, 16], organic light-emitting diodes (OLEDs) [17, 18] and organic photovoltaics (OPVs) [13, 19, 20]. In addition, some passive components such as conducting tracks, resistors and capacitors are also being fabricated from organic materials creating the potential for all-organic electrical circuits [21–23].

OTFTs are an exciting class of devices within the organic electronics field. The prospect of low cost organic electronic modules incorporating OTFTs fabricated at low temperatures using low energy techniques is very attractive [24]. Low temperature solution-based processes, such as ink-jet printing, allow for compatibility with flexible substrates, upon which it would be impossible to fabricate conventional electronics. In addition, conducting polymers can be synthesised in a laboratory without using rare or expensive materials meaning that they have the potential to be low cost when produced on a large scale [25, 26].

The focus of the work in this thesis will be on a sub-class of OTFT devices, which take advantage of movement of ions within their dielectric layer to achieve current modulation. This intra-dielectric ionic movement is distinct from the operation of many OTFTs which are organic field-effect transistors (OFETs). Whilst organic transistors (in general) are sometimes referred to as OFETs in literature, this term implies the utilisation of an electric field to modulate the current between source and drain as in a conventional field effect transistor. Although this is the mechanism used in many OTFTs, a large number of organic transistors (including those discussed in this thesis) do not rely on a field effect but rather on other mechanisms such as ionic movement and electrochemical effects [27–29]. As such, the more generic label “OTFT” will be used to describe the organic transistors presented here.

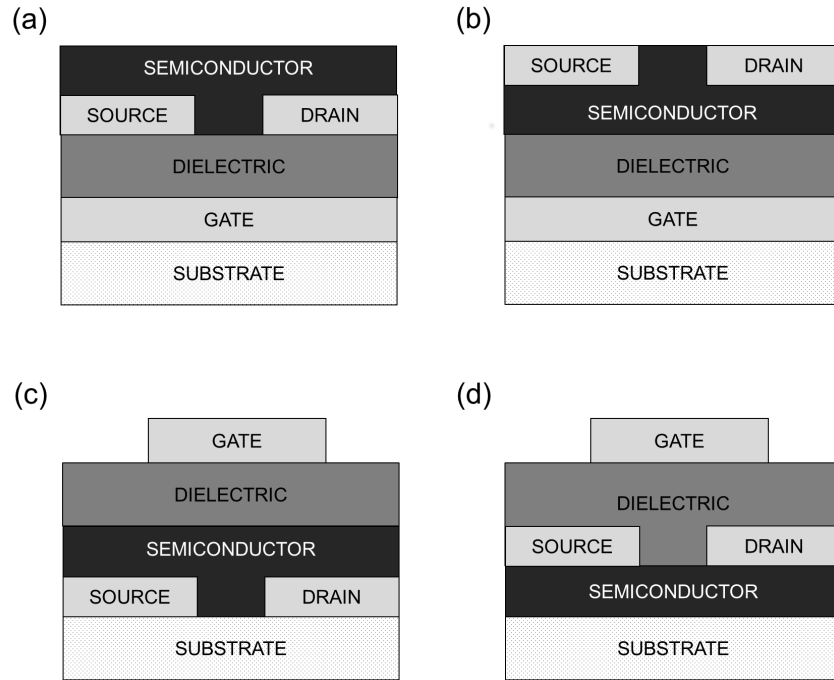


FIGURE 1.2: Common thin film transistor architectures - (a) bottom gate bottom contact, (b) bottom-gate top-contact, (c) top-gate bottom-contact, (d) top-gate top-contact.

As mentioned above, the OTFTs presented in this thesis all depend on ionic movement within their dielectric layers for current modulation (as will be shown in Chapters 3, 4 and 5). This ionic movement leads to the property which is perhaps the greatest advantage of devices of this type: their low operating voltage. Many other organic transistors show promising performance parameters, however their high operating voltage is considered a major drawback [30, 31]. On the other hand, the low operating voltage of the devices presented here makes them ideal candidates for low-power applications and amplifying small electrical signals from the transducing elements of sensors.

1.1 Device Architecture

OTFTs are generally fabricated as one of four different architecture types which are named depending on the location of the source, drain and gate electrodes relative to the semiconductor layer. These four different configurations are: bottom-gate bottom-contact, bottom-gate top-contact, top-gate bottom-contact, and top-gate top-contact (see Figure 1.2). The best configuration to employ depends on the materials used as well as the deposition and fabrication methods which are available.

The transistors presented in this thesis are all of a top-gate bottom-contact configuration. This architecture is used for several reasons, the foremost of which is that the source and drain electrodes have been pre-patterned via laser etching on glass slides to achieve a well-defined and consistent source-drain electrode separation of of 20 μm . Since the top-gate bottom-contact configuration has the source and drain electrodes directly adjoined to the substrate, it suits this type of pre-patterning. Details of the fabrication methods and the materials used will be further discussed in Chapter 2.

1.2 Conventional Thin-Film Transistor Operation

Thin-film transistors (TFTs) are devices which can modulate the current into one terminal (the drain) by modulating a signal at another terminal (the gate). They are useful for signal amplification, modulation or switching. A basic description of the operation of conventional TFTs will be provided in this section for the purposes of comparison with the OTFTs presented later in this thesis. It will be assumed that the devices are enhancement mode TFTs with a p-type semiconductor. Figure 1.3 shows a diagram of a TFT with its voltage and currents labelled as follows: drain-source voltage (V_{DS}), gate-source voltage (V_{GS}), drain current (I_D), source current (I_S) and gate current (I_G).

Conventional inorganic TFTs employ an insulating dielectric layer (commonly silicon dioxide in the case of inorganic devices [32]) across which an electric field can be established. The magnitude of this electric field is determined by the level of V_{GS} . Depending on the strength of this electric field, more (or fewer) charge carriers in the semiconductor layer will be attracted to the semiconductor-dielectric interface forming a region whose conductivity depends on V_{GS} ; the stronger the electric field, the more charge carriers will be attracted to this area. Due to the dielectrics used in such devices being electrically insulating materials, I_G is very low and hence drain current $I_D \approx I_S$.

In a device with a p-type semiconductor, when V_{GS} is more positive than a certain level called the threshold voltage (V_{TH} - see Section 1.3.3 below), the device is said to be off and I_D is largely related to the dimensions of the devices and the base conductivity of the semiconductor material (Figure 1.4(b)) [33]. V_{TH} is the voltage required at the gate electrode for the positive majority charge carriers (holes) to start accumulating at the semiconductor-dielectric interface and the conductivity of the source-drain channel (the region of semiconductor lying between the source and drain electrodes) to start increasing. When V_{GS} is more negative than V_{TH} (i.e. $|V_{GS}| > |V_{TH}|$), the transistor is operating in either one of two regimes: linear or saturation. If $|V_{GS}| > |V_{TH}|$ and $|V_{DS}| < |V_{GS}|$, the device is said to be in the linear regime (Figure 1.4(c)). That is, for a fixed V_{GS} , I_D varies linearly with V_{DS} (the channel acts as a resistor). On the other hand, if $|V_{GS}| > |V_{TH}|$ and $|V_{DS}| > |V_{GS}|$, the device is in saturation, and I_D no

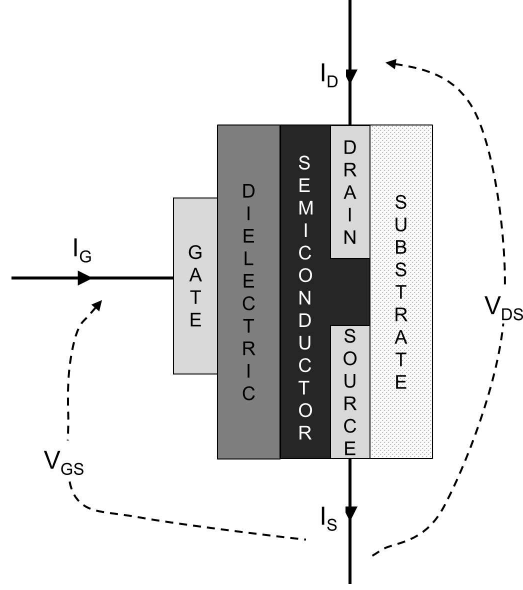


FIGURE 1.3: Diagram of a TFT, with the relevant voltage and currents labelled. By convention, voltages are referenced to the source electrode.

longer depends on V_{DS} but is approximately constant for a given V_{GS} . Physically, I_D saturates because when $|V_{DS}| > |V_{GS}|$, the positively charged holes are more attracted to the drain than the gate and the position of the accumulated charge carriers changes such that the channel between the source and drain becomes comprised of a region of higher conductivity near the drain as well as a region of lower conductivity near the source (see Figure 1.4(d)). Subsequent increases in $|V_{DS}|$ in the negative direction are compensated for by a further change in the position of the accumulated charge carriers towards the drain such that the total resistance of the channel also increases and so I_D , ideally, remains constant.

The following equations are an approximation of the behaviour of conventional TFTs in terms of I_D :

$$I_{D,LIN} = (W/L)C_i\mu(V_{GS} - V_{TH})V_{DS} \quad (1.1)$$

$$I_{D,SAT} = (W/2L)C_i\mu(V_{GS} - V_{TH})^2 \quad (1.2)$$

where $I_{D,SAT}$ is the saturation drain current, $I_{D,LIN}$ is the linear region drain current, W is the channel width, L is the channel length, C_i is the per-area capacitance of the dielectric layer [34]. Figure 1.5(a) shows a modelled version of the output characteristic of a TFT using these two equations along with linear interpolation to estimate

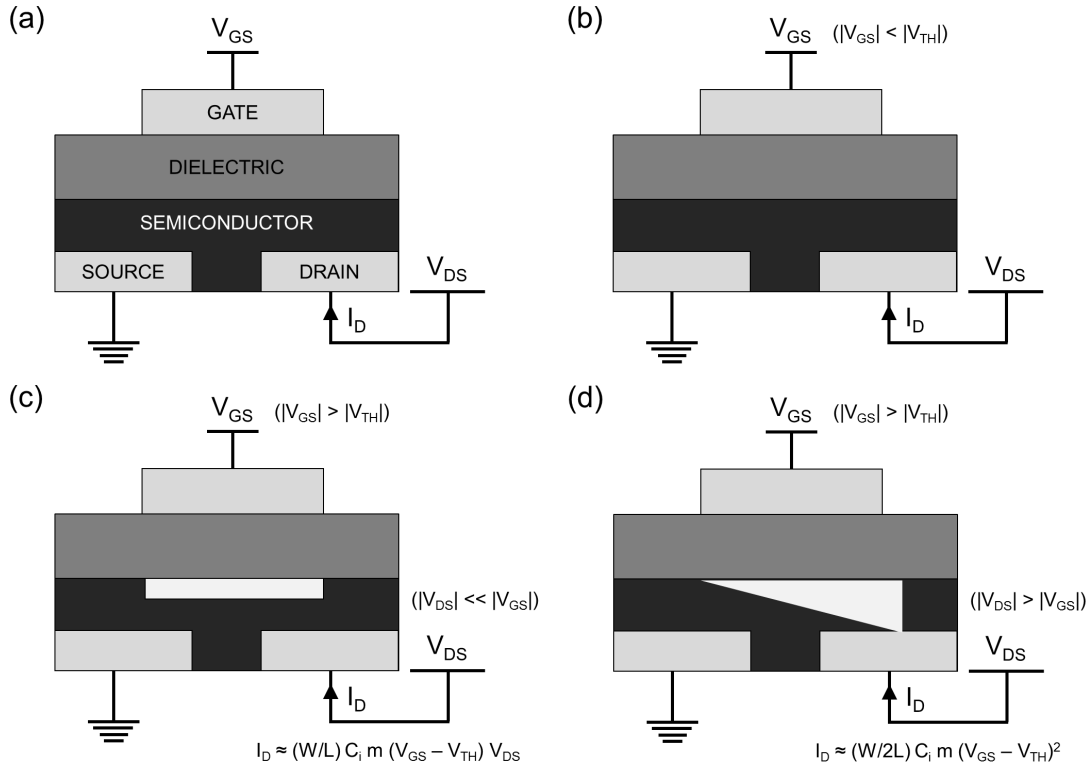


FIGURE 1.4: Pictorial description of the operation of a TFT: (a), labelled diagram; (b), “off” state; (c), linear regime; and, (d), saturation regime. The white region within the semiconductor in (c) and (d) is a region of high conductivity induced by the electric field established by V_{GS} .

the current between the two modes of operation.

Although Equations 1.1 and 1.2 describe the behaviour of field effect-dependant devices, the output characteristics of the devices presented in this thesis (which rely on ionic movement rather than a field effect) also show a similar behaviour to this model, with clearly defined linear and saturation regions. Therefore, the model is still useful for the OTFTs discussed later since concepts such as V_{TH} are still relevant to determine the required operating voltages, and the device dimensions (i.e. W/L) will still affect their characteristics. However, since it is shown in Chapter 3 and beyond that electrochemical mechanisms, as well as intra-dielectric ionic movement, contribute to current modulation in the devices presented here, using the ion-enhanced capacitance value as C_i to relate I_D to device dimensions, bias voltages and semiconductor properties (i.e. μ) is not a valid method for these devices, so other more direct methods must be used to characterise them.

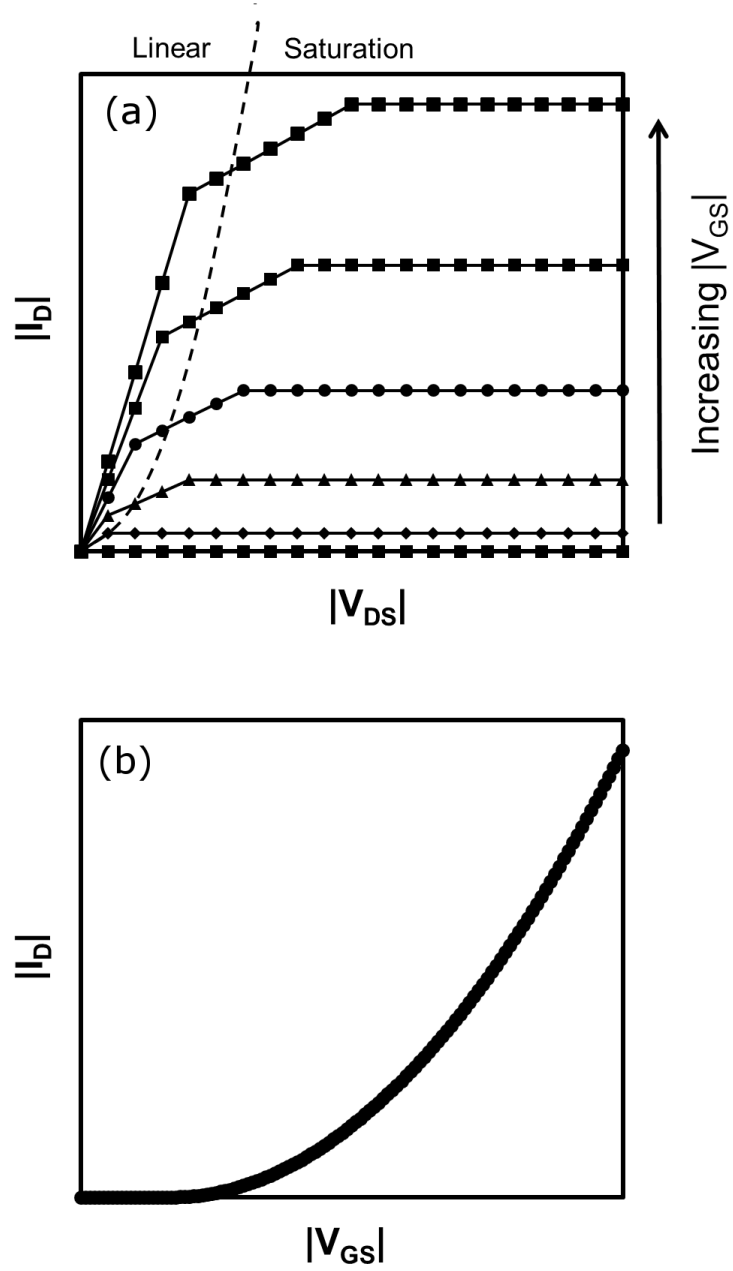


FIGURE 1.5: Example of (a) an output characteristic and (b) a transfer characteristic for a TFT as modelled by Equations (1.2) and (1.1).

1.3 OTFT Performance Parameters

There are several different parameters by which the performance of OTFTs are measured and compared. In the field of OPVs, it is usually sufficient to compare devices using only one parameter - the power conversion efficiency [35, 36]. However, when characterising transistors, it is not possible to assess all of the advantages and disadvantages of a given device via the numerical comparison of a single parameter. Indeed, there are many aspects to the behaviour of OTFTs which need to be considered when comparing them - not all of which are quantitative. Nonetheless, it is often of some use to compare devices of a similar structure or those which employ the same materials parametrically. It should be noted that the parameters mentioned in this section are not exclusively used to describe the performance of OTFTs; inorganic devices also use the same measurements.

1.3.1 Charge Carrier Mobility

Possibly the most often quoted parameter in literature when comparing the performance of OFETs or OTFTs in general is the charge carrier mobility (μ) of the semi-conducting layer [10, 15, 37]. This is a coefficient relating the drift velocity (v_d) of charge carriers within the material to an applied electric field (E) as follows:

$$v_d = \mu E \quad (1.3)$$

In other words, the higher the charge carrier mobility of a material, the faster charge carriers can move within it under a given electric field. μ is commonly measured in $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (rather than the SI unit of $\text{m}^2\text{V}^{-1}\text{s}^{-1}$).

In field-effect devices, μ is usually calculated from either of the two equations approximating I_D in TFTs (Equations (1.2) and (1.1)) when all the other parameters are known. In devices where a field effect is not employed to realise current modulation, such as those presented in this thesis, another technique must be used to determine μ . Time-of-flight (TOF) techniques involve directly measuring the time taken for a charge to travel between a certain distance through a material under an electric field. TOF measurements typically involve exciting charge carriers with incident photons and measuring the time taken for the charges to reach the electrodes which provide the electric field [38].

It is widely regarded that the charge carrier mobility of an organic semiconductor depends on its morphology [39]. Such a dependence is thought to be due to defects and grain boundaries being common sites for charge traps in both small molecule and polymeric semiconductors [40–42]. As such, much research is conducted trying to control the morphology of semiconductor films in OTFTs, and there are a variety of methods being developed to achieve this [39, 43, 44].

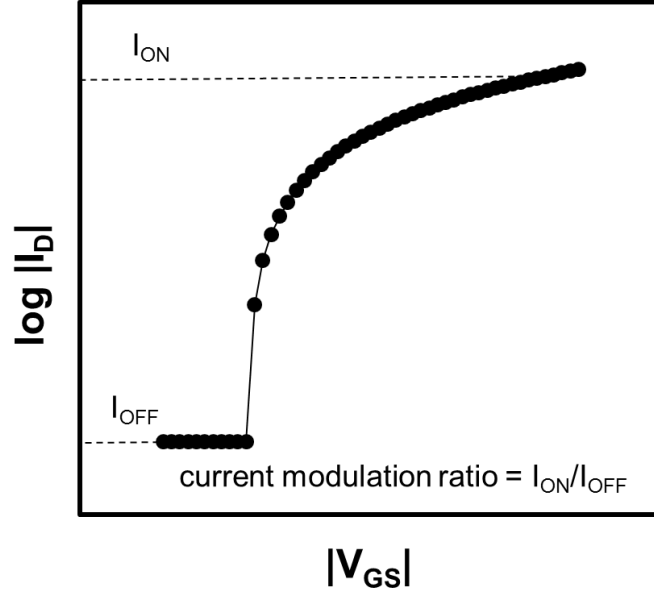


FIGURE 1.6: Determining current modulation ratio from a transfer curve.

Calculations of mobility are not conducted within this thesis, however it is important to realise that the ability of charges to move within the semiconductor layer is a significant property when it comes to the electric characteristics of devices.

1.3.2 Current Modulation Ratio

Another performance indicator of OTFTs is the current modulation ratio (I_{ON}/I_{OFF} - also known as the “on-to-off ratio”). This parameter represents the amount by which the transistor can change its output current (I_D) due to a change in V_{GS} for a given V_{DS} . In general, it is desirable to maximise I_{ON}/I_{OFF} as it is the limiting factor for the magnitude by which a signal can be amplified or switched.

Typically, I_{ON}/I_{OFF} is calculated by choosing V_{DS} so that the device is in the saturation region and then selecting two values of V_{GS} : one where the device is at or close to its minimum I_D (“off”) and one where it is close to its maximum I_D (“on”) (see Figure 1.6). For conventional amorphous silicon devices in commercial use, this value is typically of the order of 10^8 [34, 45]. For organic devices, I_{ON}/I_{OFF} varies greatly, but may be as high as 10^6 for OTFTs based on the widely-used polymer poly(3-hexylthiophene) (P3HT) or as high as 10^8 with pentacene-based devices [10].

The current modulation ratio is the parameter of most interest for the experiments performed in Chapters 3, 4 and 5. In these chapters, the devices are studied and the dielectric materials varied in an attempt to maximise I_{ON}/I_{OFF} .

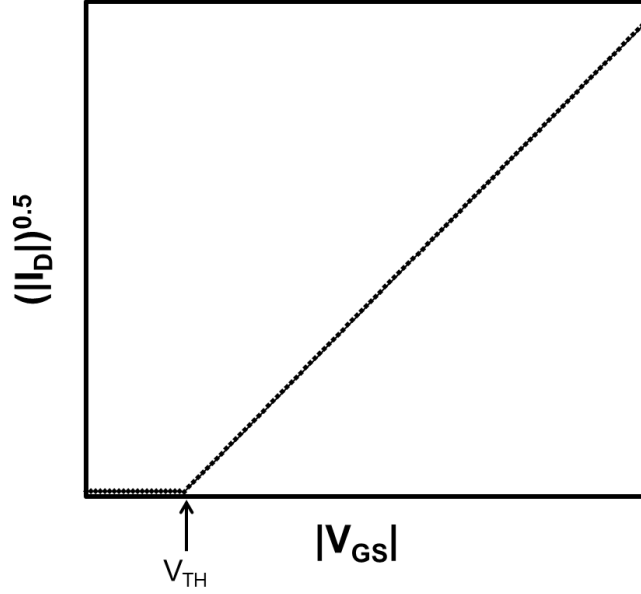


FIGURE 1.7: Illustration of using the graphical method for approximating V_{TH} .

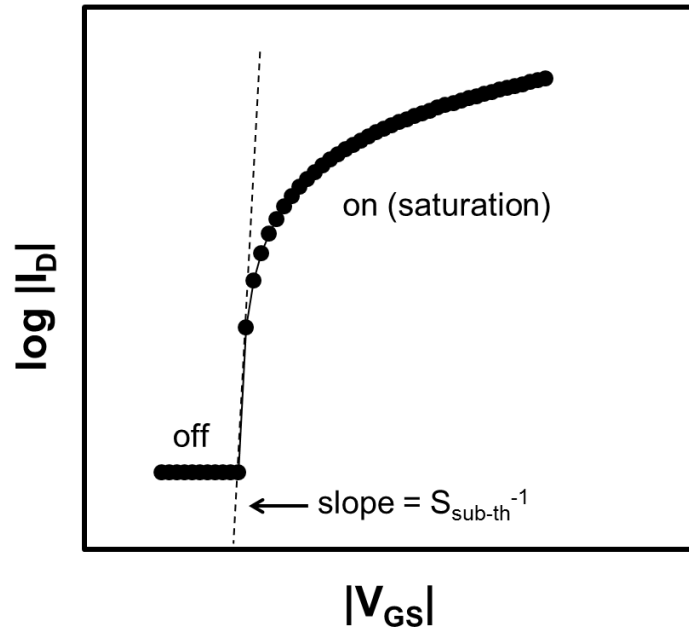
1.3.3 Threshold Voltage

The threshold voltage (V_{TH}) is the value of V_{GS} required to start turning on conductance in the source-drain channel of the transistor. For OTFTs based on a p-type semiconductor, V_{TH} is usually negative, with further turn-on facilitated by a more negative V_{GS} . On the other hand, for devices employing an n-type semiconductor, V_{TH} is usually positive [46, 47]. In the literature of organic transistors, the term "turn-on voltage" is sometimes used instead of "threshold voltage" [48, 49] due to the latter having its origins in inorganic field-effect devices [34]. In this thesis, however, " V_{TH} " will be used to denote this parameter.

The V_{TH} of an OTFT is usually determined graphically by plotting $(|I_{DS}|)^{1/2}$ as a function of V_{GS} , and fitting an approximation to the linear section of the graph. From Equation (1.2), we have:

$$(|I_{DS}|^{1/2}) = \alpha(V_{GS} - V_{TH}) \quad (1.4)$$

where α is a constant depending on the other parameters of Equation (1.2). We can now determine that V_{TH} is given by the intercept of the linear approximation of $(|I_D|)^{1/2}$ as a function of V_{GS} with the V_{GS} axis.

FIGURE 1.8: Graphical method for approximating S_{sub-th} .

V_{TH} is a determinant of the operating voltage of the device and lower values (in magnitude) are usually desired.

1.3.4 Sub-threshold Swing

Sub-threshold swing (S_{sub-th}) is a measure of the change in V_{GS} required to change I_{DS} by an order of magnitude (measured in V/decade) in the region where the device is switching between “off” and “on” (also known as the sub-threshold region). The lower the value of S_{sub-th} , the more sensitive the transistor is. S_{sub-th} can be determined by plotting the transfer characteristic on a semi-logarithmic scale and taking the inverse of an approximation of the slope in the region when the device is turning on.

S_{sub-th} is an important parameter both in relation to switching and signal amplification applications. When a device is used as a switch, a low S_{sub-th} value is important to achieve a clear differentiation between the “on” and “off” states for a small change in V_{GS} . In logic gates, for example, a large change in current for a relatively small change in V_{GS} is necessary due to the relatively low supply voltages used. When using a transistor to amplify a signal, the transistor generally operates in the sub-threshold region, so the S_{sub-th} is a limiting factor on how large the transconductance of the amplifier stage can be.

1.3.5 Other Parameters

There are some other important factors of OTFT operation to consider when characterising devices which are not usually quoted as key performance parameters. These include: the ratio of I_G to I_D , contact resistance between the source and drain electrodes and the semiconductor, as well as the maximum operation frequency or switching speed of the device.

If I_G is a significant fraction of I_D , the device can be considered to not be an effective transistor because the input resistance of the gate is too low. If OTFTs with a relatively high I_G are cascaded together, the current drawn through the gate of each device will mean make it difficult to construct a useful switching circuit or amplifier.

Too high of a contact resistance between the source and drain electrodes and the semiconducting layer creates a significant series resistance between the source and drain resulting in the resistance, rather than the transistor, dominating the electrical properties.

The maximum operating frequency of the device depends on the mechanisms involved in current modulation [50], and this limits the potential applications for the OTFT. For example, a device which can switch on and off quickly (say, in the MHz range) can be used in high-speed digital circuitry and can also be used as an amplifier for high-speed analog signals. On the other hand, a device which cannot switch quickly but might have other advantages (such as low operating voltage or simple processability) could be an ideal candidate for a cheap, disposable, single-use sensor where only a binary response is required.

1.3.6 Relative Performance of OTFTs

When OTFTs were in the early stages of development, their performance was very poor when compared with conventional devices. For example, in the mid 1980s, the hole mobility of OTFTs was four or five orders of magnitude lower than that of doped amorphous silicon [15]. Nowadays though, the best small molecule or single crystal organics are approaching amorphous silicon transistors in terms of mobility and current modulation ratio [10]. Polymer-based devices, on the other hand, are still lagging behind small molecule-based OTFTs in terms of electrical performance, but have the potential advantages of low-cost and low-temperature fabrication. These issues will be discussed further in Chapter 2.

1.4 Applications for OTFTs

There are many areas in which OTFTs offer the potential for significant advantages over conventional transistors. These advantages tend to relate to two properties of organic materials: their compatibility with flexible substrates, and their potential for low-cost fabrication.

Some groups have succeeded in fabricating displays incorporating OTFTs as the switches to select the state of pixels [51–53]. Although the operating voltages can be somewhat high (up to 30 V), the displays are being fabricated on flexible substrates with practical refresh rates which should be considered a major breakthrough and is very encouraging for further advances.

Organic radio frequency identification (RFID) or other recognition devices are also receiving a lot of attention from some research groups. Since one potential use for RFID is as a replacement for barcodes on disposable product packaging, the potential for low-cost fabrication on flexible substrates makes OTFTs ideal candidates for the basis of these circuits. Fully functional organic RFID transponders on flexible substrates are already being reported [54, 55].

Organic electronic circuits are fast becoming more and more sophisticated. In a recent paper from Myny et al., 8-bit microcontrollers each comprised of 3381 organic transistors fabricated on flexible plastic films were reported. Even though the operating voltages are high ($V_{GS} = 50$ V) and the instruction speed is relatively slow (40 instructions per second) [56], developments such this show that organic electronic devices are rapidly becoming viable in many applications which require good electrical performance.

Another field of applications is in sensors. It is hoped that the research presented in this thesis can help build towards the development of OTFTs for widespread use in sensing applications in the near future.

1.5 Motivations and Aims

Research continues on improving the performance of OTFTs to rival and exceed their conventional inorganic semiconductor-based counterparts. However, somewhat less attention is paid to taking advantage of characteristics inherent to some of the materials used in OTFTs to create devices with unique properties which are desirable in specific applications at the expense of numerical parameters. The research presented in this thesis aims to develop understanding about a certain class of low operating voltage OTFTs, improve their performance and investigate their use in sensing applications.

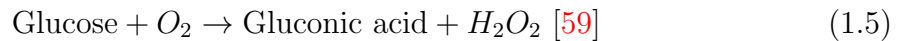
1.5.1 Characterisation and Understanding

The devices presented in this thesis belong to a certain class of OTFTs which can operate at low voltages due to ionic movement within them. Initially, devices similar to those reported by the group of Österbacka [27, 48, 49, 57] were fabricated and investigations into the mechanisms involved in their operation were conducted. Subsequently, changes to the materials used in the devices were made with the goal of improving their performance and sensitivity.

1.5.2 Glucose Sensing

With the global increase in the incidence of diabetes, the demand for glucose-sensing devices has grown rapidly in recent years. The number of adult sufferers of diabetes worldwide was estimated to be 284.8 million (or 6.4 % of all adults) in 2010 and this is predicted to rise to 438.7 million (7.7 %) by 2030 [58]. Sufferers of diabetes must frequently measure their blood sugar level - typically several times per day - to provide themselves with adequate monitoring and control. However, measurement of blood glucose levels can be quite an invasive process; it usually involves taking a small sample of blood from the finger. As a result, there is a lot of interest in non-invasive blood glucose level measurement techniques.

Glucose oxidase (GOX) is an enzyme which selectively catalyses the oxidation of glucose in the following way:



and its specificity makes it an ideal recognition element for a glucose sensor. Several other studies have already been conducted on sensors using GOX as the recognition element in organic devices; however they have the downside of operating at high voltages, involving complex fabrication techniques or require complex external circuitry such as an electrochemical cell [60–62]. The simplification of sensors of this type into a single device with a recognition element (in this case GOX) and an electrical transducer (the OTFT) contained in one device is another of the aims of the work presented here. Transistors have already been shown to have advantages over devices like chemiresistors in term of sensitivity [28] making the OTFTs presented here solid candidates for the foundation of a sensing platform. Furthermore, the high biocompatibility of enzymes with some organic materials [63, 64] means that organic devices have the potential for very high sensitivity.

2

Experimental Procedure and Materials

The techniques and methods used to fabricate and characterise the OTFTs presented in this thesis will be explained in this chapter. Firstly, though, a short explanation of the choice of device architecture and materials common to most devices discussed here will be included. Other materials used will be introduced as they arise in subsequent chapters.

2.1 Device Architecture

As mentioned in Chapter 1, the OTFTs presented here are all of top-gate bottom-contact configuration. In Section 2.2.2, it will be explained that the use of this architecture is largely due to the reliance on pre-patterned ITO for the source and drain electrodes, which requires selecting a configuration with these electrodes adjacent to the substrate.

The compatibility of solvents also needs to be considered when designing the architecture of the device. For example, when a film is deposited on another film (in this case the PVP dielectric on top of the P3HT semiconductor, or the PEDOT:PSS gate on top of the dielectric), it is important that the existing film is not re-dissolved by the next solvent. In other words, the use of orthogonal solvents is required to ensure non-dissolution of layers deposited previously [65].

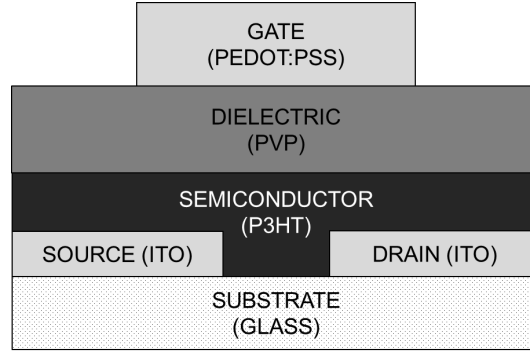


FIGURE 2.1: Basic device architecture and materials used.

2.2 Materials

This section will introduce the materials used in a “standard OTFT”, which is defined in this thesis as being of the configuration shown in Figure 2.1. The fabrication procedure is described below in Section 2.3. These devices are similar to those introduced in a series of papers in 2004 and 2005 by the group of Österbacka [27, 48, 49, 57]. The devices presented by this group rely on the hygroscopic nature of the dielectric, which attracts water into the device, and the subsequent movement of H^+ ions at relatively low V_{GS} values to modulate the current between source and drain. This type of device was of interest for the direction of this project primarily due to the low-voltage operation. What is known of the mechanism will be discussed in Chapter 3. One of the aims of the work presented in Chapters 4 and 5 is to improve the performance of the device through maintaining the low-voltage operation whilst improving the current modulation ratio and S_{sub-th} parameters by the introduction of other materials in the dielectric layer. These other materials which are used only in variations of the basic device will be introduced and discussed in the chapters in which they appear.

2.2.1 P3HT

Poly-3-hexylthiophene (P3HT) is one of the most widely used semiconducting polymers in organic electronics nowadays. It can be employed in OPVs in conjunction with an n-type organic semiconductor to make efficient bulk-heterojunction and bi-layer solar cells [66, 67] and can be used as a light-emitting material in OLEDs [68]. Furthermore, devices made with P3HT semiconducting layers are amongst the highest-performing OTFTs with polymeric active layers [10]. Table 2.1 shows a comparison of reported mobility values of transistors using P3HT and a selection of other high-performance organic semiconductors. For interest, there is also a comparison with some inorganic semiconductors of morphologies related to the organic examples.

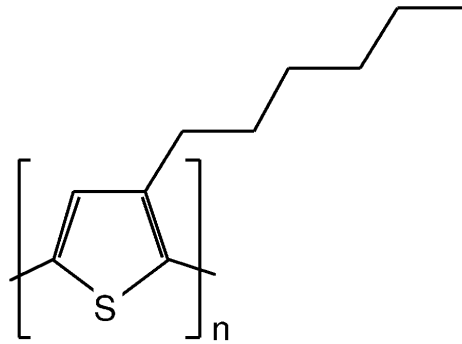


FIGURE 2.2: P3HT chemical structure.

Mobility Values of Organic and Inorganic Semiconductors of Different Crystallinities in OTFTs ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)		
Morphology	Organic	Inorganic
Single Crystal	40 (rubrene) [69]	1000 (silicon) [70]
Polycrystalline / Small molecule	3 (pentacene on a PVP co-polymer) [10], 1.5 (pentacene on SiO_2) [10]	65 (silicon) [70]
Amorphous / Semicrystalline Polymer	0.1 (P3HT) [10]	1 (amorphous silicon) [70]

TABLE 2.1: Mobility values of several organic and inorganic semiconductors in OTFTs.

The main reasons for selecting P3HT for the OTFTs in this study were its high processability and its high charge carrier mobility compared with other polymeric semiconductors. Since one of the aims of this project is to use OTFTs which can be fabricated using simple, low-temperature methods in air, techniques such as thermal evaporation are not suitable. P3HT, being soluble in common solvents (in this case, chloroform) allows for spin coating in air. Furthermore, the fact that it is a well studied material removes an unwanted layer of complexity to this study. Since the research presented here is purely related to characterising and understanding the transistors themselves, it is sensible to use a material with an existing knowledge base and build upon that rather than look to newer materials. Like many high-performance polymeric semiconductors, P3HT is a majority hole material.

The chemical structure of P3HT can be seen in Figure 2.2. Before P3HT became widely used as a semiconductor in organic electronics, there had already been some success with polythiophene being used as a semiconductor in OTFTs, prepared by electrochemical methods [71, 72]. However, the addition of alkyl chains vastly increased solubility and since then, the use polyalkylthiophenes deposited from solution

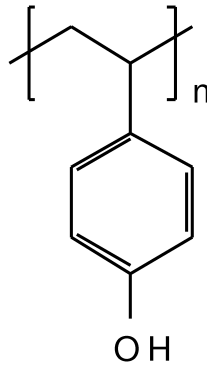


FIGURE 2.3: PVP chemical structure.

has become widespread.

There is a great deal of research being reported in literature related to maximizing the mobility of P3HT films. For example, most solution-deposited polymer thin films have low ordering which reduces their mobility [34]. In such cases, mobility can be increased by doping the semiconductor, but this also reduces the current modulation ratio of the transistor.

The P3HT used in this study was sourced from Luminescence Technology Corp., Taiwan, and had a quoted regioregularity of 95 % and a molecular weight of 55 000 to 60 000 g/mol.

2.2.2 PVP

Poly(4-vinylphenol) (PVP) is a polymeric dielectric material which is widely used in organic transistors [73]. Often, when used in as the dielectric in an OTFT, the PVP layer is cross-linked to improve its dielectric properties [74, 75]. When it is cross-linked, PVP behaves as a conventional insulator across which an electric field can be induced and, as such, transistors with cross-linked PVP films are FETs. However, most cross linking methods require high temperatures, which is contrary to the design goals of this project. Furthermore, this project aims to take advantage of the nature of non-cross-linked PVP films which allow for ionic movement within them which facilitates low-voltage OTFT operation.

It has been found by Bäcklund et al. that the thickness of the PVP dielectric has little effect on the output characteristic of the devices in which the PVP is not cross-linked and the PVP is hygroscopic. In a conventional FET, I_D depends directly on the thickness of the dielectric layer. This lack of dependence is one of the pieces of evidence to show that the mechanism involved in modulating current in these devices

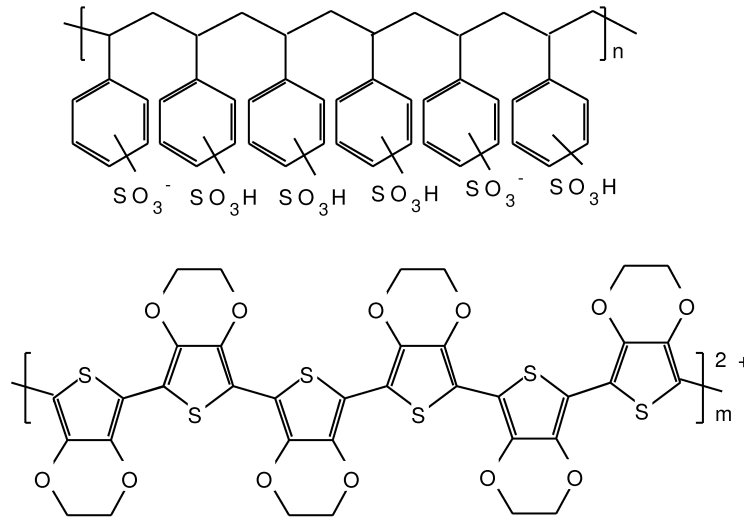


FIGURE 2.4: PEDOT:PSS structure.

is not an electrical field effect [57].

2.2.3 PEDOT:PSS

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is possibly the most widely-used organic conductor in organic electronics. Its molecular structure is shown in Figure 2.4. It is highly conductive with conductivity up to 1000 S/cm [76]. Its applications include: forming low-resistance contacts in organic electronic circuits [21] and being deposited as thin films in some organic photovoltaic devices to provide a transparent interface layer between the active layer and the anode [77].

PEDOT:PSS has been chosen for the gate electrode in these OTFTs due to its high conductivity, robustness and processability. Other conducting organic materials that could have been chosen for this layer of the device include graphene, which suffers from poor processability, or metallic nanoparticles.

As mentioned below, PEDOT:PSS could also be used for the source and drain electrodes of the types of devices presented in this thesis if an appropriate deposition method were available to create the desired channel dimensions.

2.2.4 ITO

Indium-tin-oxide (ITO) is a widely-used material in OPVs [66], OLEDs [78] and other applications which require transparent electrodes. It has very low resistivity - as low

as $2 \times 10^{-4} \Omega \text{ cm}$ when deposited on glass [79]. ITO is used in this study for the source and drain electrodes of the OTFTs. This is primarily due to the fact that researchers in our group working on OPVs use pre-patterned ITO on glass substrates, which are accurately patterned by the supplier. Ordering these type of pre-patterned substrates for OTFTs as well is an easy way to ensure consistent channel dimensions. Previously, attempts were made to pattern ITO on glass using photolithography and wet etching, but under this method it was difficult to consistently achieve a channel of the dimensions required.

Since there is no need for transparent electrodes in these OTFTs, we can potentially look to other materials in any future work for source and drain electrodes. Additive processes such as ink-jet printing of dispersions of the conducting polymer PEDOT:PSS (see below) are suitable for this so long as the required channel dimensions are achievable.

2.3 Fabrication

The fabrication procedure for a standard OTFT will be described here. We have defined a “standard OTFT” here as having a top-gate bottom-contact architecture using the following materials: glass substrate, ITO source and drain electrodes, P3HT semiconductor, PVP dielectric and PEDOT:PSS gate.

As mentioned above, all standard devices were fabricated on glass substrates with pre-patterned indium-tin-oxide (ITO) source and drain electrodes from Kintec. The channel length and width is $20 \mu\text{m}$ and 3 mm respectively. P3HT (Lumtec) was dissolved in chloroform at a concentration of 20 mg/mL . An approximately 100 nm thick P3HT layer (as measured by profilometry) was spin-coated at 2000 rpm for 60 s . This film was then patterned manually to expose the source and drain electrodes and to allow enough space for the over-lapping PVP layer and was then annealed for 15 minutes at 45°C in air to remove an excess solvent. PVP (Aldrich) was dissolved in ethanol at a concentration of 80 mg/mL . The dielectric layer was spin-coated for 60 s at 2000 rpm to form a film with a thickness of approximately 500 nm and patterned manually. The P3HT/PVP two-layer structures were annealed at 85°C in air to remove any remaining solvents. Lastly, PEDOT:PSS (Aldrich) was drop-cast on the top of gate dielectric layer and dried on a hot plate at 40°C in air. Fabricated devices were typically characterised in air immediately after drying the PEDOT:PSS layer.

The step which has the most propensity for variations in this fabrication method is the drop-casting of the PEDOT:PSS gate and effects of this will be discussed in Chapter 3.

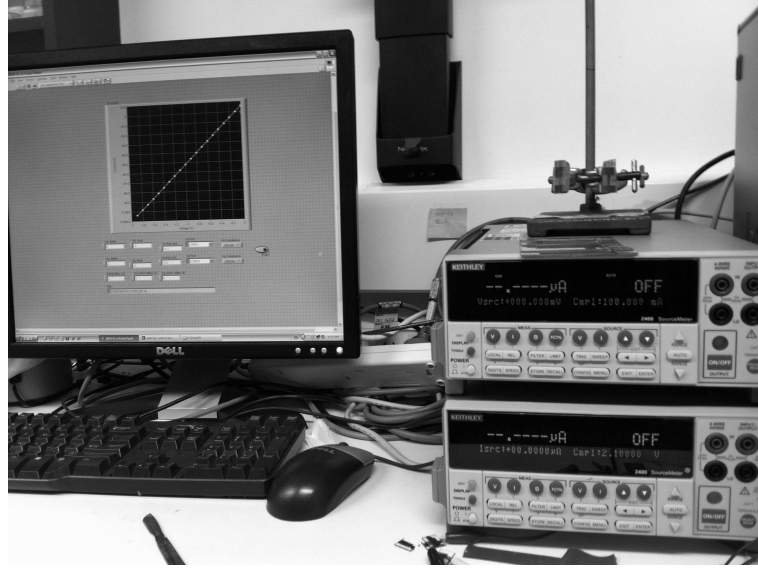


FIGURE 2.5: Photograph of two Keithley 2400 SourceMeters connected to a PC running LabVIEW.

2.4 Characterisation

The various techniques and equipment used in the different aspects of device characterisation will be discussed in this section.

2.4.1 Output Characteristic

The output characteristic is a plot of I_D as a function of V_{DS} for a series of V_{GS} values (see the example given in Figure 1.5(a)). Output characteristics for the transistors were measured using two Keithley 2400 SourceMeters controlled by a program written in National Instruments' LabVIEW development environment. For a given value of V_{GS} , V_{DS} was swept over a specified range and both I_D and I_G were recorded. This was repeated for a series of different V_{GS} .

The I_G (gate current or leakage current) values recorded in this measurement are useful for comparing the I_D to I_G ratio or how much I_G is contributing to the total current through the source electrode of the devices.

2.4.2 Transfer Characteristic

The transfer characteristic is a plot of I_D as a function of V_{GS} for a given value of V_{DS} (see the example given in Figure 1.5(b)). It is usually presented on a semi-logarithmic set of axes to facilitate a more informative representation of lower values of I_D (on

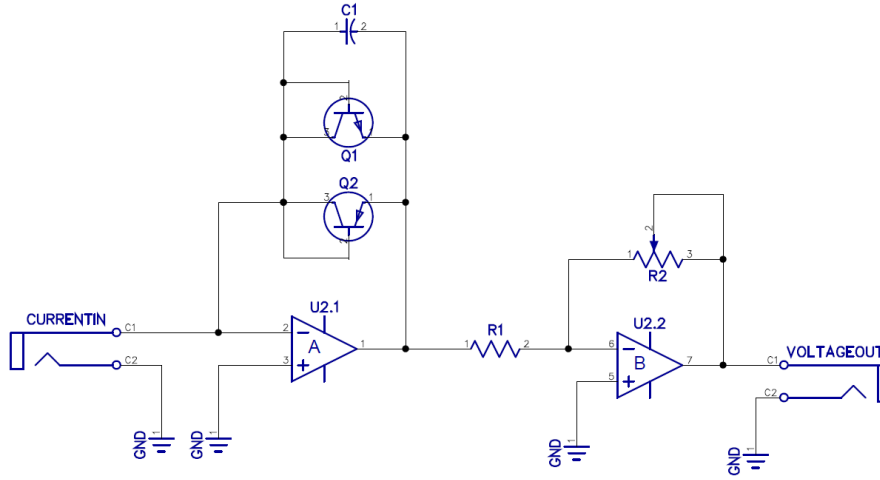


FIGURE 2.6: Simplified circuit diagram of custom transimpedance amplifier with a logarithmic response.

a linear scale relatively low value become unreadable). This data was collected in a similar method to the data for the output characteristic, with a LabVIEW program controlling the two Keithley SourceMeters. For a fixed value of V_{DS} , I_D is measured as V_{GS} is swept over a range of values. V_{GS} is usually swept both “forwards” and “backwards” (i.e. firstly in the negative direction, and secondly in the positive direction or vice versa). A “quasi-transfer curve” can also be constructed from data taken when measuring the output characteristic, and plotting I_D as a function of V_{GS} instead of V_{DS} . Transfer characteristics of this indirect type are also presented in some parts of the results chapters, and despite having necessarily less data points than the directly measured transfer curves, they can still be a useful way to quickly illustrate the performance of a device.

Examining the transfer characteristic is the simplest way to approximately determine the current modulation ratio and the value of V_{GS} for which the devices begin to turn on (V_{TH}).

2.4.3 Time-domain Measurements

Measurements of current were taken as a function of time in order to gain an understanding of how devices perform in the time domain. The source current (I_S) was converted to a voltage by a custom logarithmic current-to-voltage (transimpedance) converter (Figure 2.6), and this voltage was then read by a National Instruments USB-6009 data acquisition (DAQ) module. The logarithmic nature of the current-to voltage converter means that current over a wide range of current magnitudes can be measured by the DAQ module. Using this method, samples were taken at speeds up to 1 kHz.

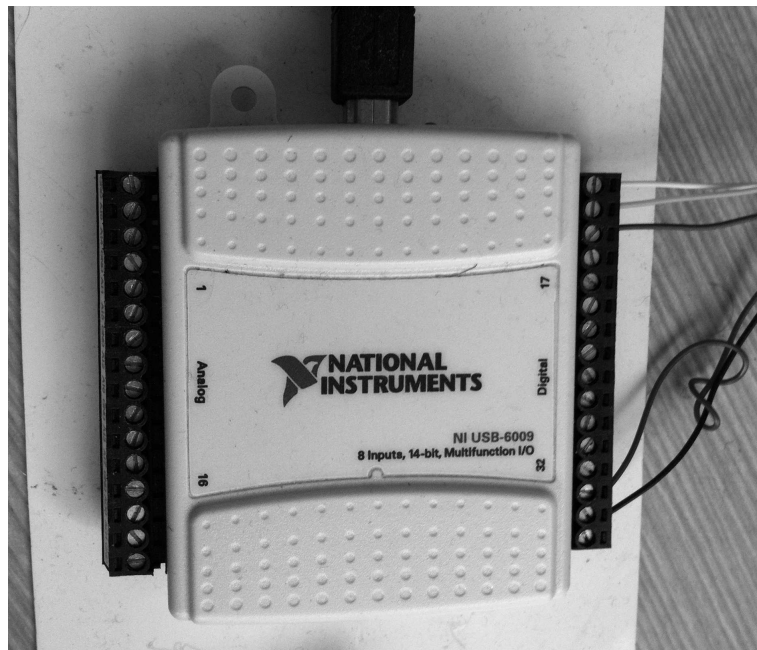


FIGURE 2.7: Photograph of National Instruments USB-6009 data acquisition module used for time-domain measurements.

2.4.4 Profilometry

Profilometry is a technique used to measure the depth profile of a sample along a one-dimensional line of the surface. A stylus is scraped across film or other sample and the depth is recorded. Profilometry is used in this thesis to measure the thickness of films deposited by spin coating. This measurement is conducted by spinning a film onto a glass substrate and scratching or wiping a void in the film. The height difference between the substrate and the top of the film then gives the thickness of the film. The profilometer used is a KLA Tencor Alpha-Step 500.

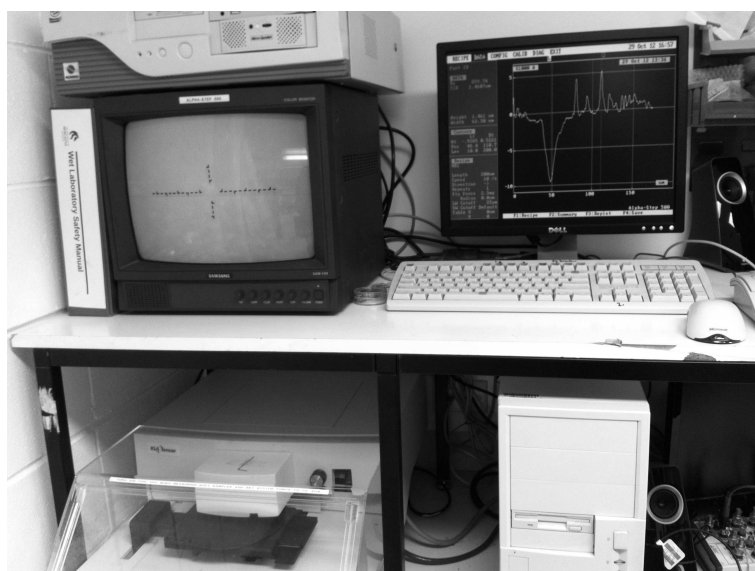


FIGURE 2.8: Photograph of KLA Alpha-Step 500 profilometer (bottom left) connected to PC and two monitors.

3

Low Operating-Voltage Organic Thin Film Transistors: Characterisation and Mechanism Investigations

In this chapter, the performance and mechanisms involved with the devices defined previously (in Section 2.2) as “standard OTFTs” will be investigated and discussed. Transistors of this type have the advantage of both low operating voltages (the advantages of which will be discussed below) and the potential for all-polymer fabrication on flexible substrates.

Low-voltage operation is important for many potential applications of OTFTs, making it one of the most desirable of device properties. For example, if the transistors were used in sensing applications, they may require portable power solutions such as batteries. In battery-powered applications, power consumption is critical and devices requiring many tens of volts to operate are not suitable. The need for such a high voltage to be supplied to the transistors would require either many batteries, which are expensive and bulky, or step-up voltage converters, which would result in unnecessary power losses. Furthermore, if OTFTs were to replace conventional transistors in digital electronics applications, they would need to be compatible with the existing logic families (such as CMOS or TTL) and other hardware, which often run from a supply of 5 V or lower.

Organic transistors which rely on a field-effect for current modulation (organic field-effect transistors, or OFETs) operate using the same mechanism to conventional field effect transistors (FETs): an electric field is established across their dielectric layer due to an applied V_{GS} , which in turn manipulates the density of charge carriers between source and drain in the semiconductor. Conventional FETs have current modulation

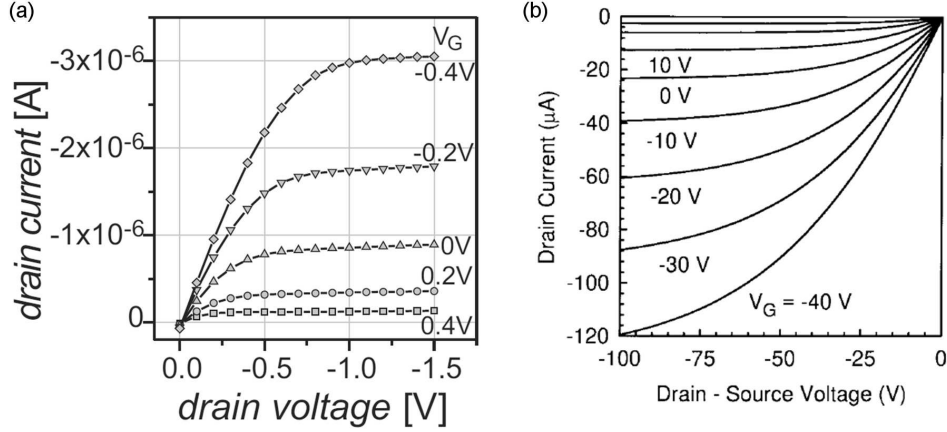


FIGURE 3.1: Typical output characteristics for (a), a “HIFET” device (reprinted from [27]) and, (b), a typical pentacene-based OFET with a SiO_2 dielectric (reprinted from [86]).

ratios in excess of 10^8 , and can operate at low voltages, with V_{TH} values in the order of a few volts [34]. Many types of OFET which use high-mobility organic semiconductors along with inorganic dielectric layers and metal electrodes exhibit current modulation ratios of the same order as their conventional counterparts, however they usually require much higher V_{GS} and V_{DS} values to achieve this [15]. Figure 3.1 shows an OTFT which utilises a hygroscopic dielectric material to achieve low-voltage operation compared with an OFET with a more conventional field-effect current modulation mechanism and a much higher operating voltage; as high as $V_{GS} = -40$ V and $V_{DS} = -100$ V to achieve full turn on.

Much research has been undertaken in recent years in an attempt to develop OTFTs with low operating voltages, with a popular approach being to utilise ionic movement within the dielectric layers of devices. One method, reported by Panzer et al. from the group of Frisbie, shows that devices with a lithium salt-doped poly-ethylene oxide (PEO) dielectric can achieve current modulation ratios up to 10^6 at $|V_{GS}| \leq 3$ V, depending on the semiconductor and device architecture used [80–82]. Xia et al. of Frisbie’s group have also used an “ion gel” (comprising an ionic liquid encapsulated within a polymeric material) as a dielectric in devices which show I_{ON}/I_{OFF} ratios of approximately 10^5 operating with a supply voltage of less than 2 V. Basic logic elements and other simple components using the ion gel-gated devices have been successfully fabricated [83]. Another type of device exhibiting low voltage operation, which was introduced by the group of Österbacka et al., is an OTFT employing the hygroscopic dielectric poly-4-vinylphenol (PVP), which is thought to facilitate the presence of ions in the device through the attraction of moisture, thereby enhancing current modulation. Such devices have shown high performance, with I_{ON} being reached at $|V_{GS}| \leq 1$ V [27, 48, 49, 57, 84, 85] (see Figure 3.1(a)).

Early work on hygroscopic insulator field-effect transistors (HIFETs) established that OTFTs with PVP dielectric layer operate effectively at low voltages, as well as determining the dependence of their devices to achieve this low-voltage current modulation on humidity (or more specifically, the presence of polar solvent molecules) [27]. Two possible mechanisms were proposed for current modulation: (1) drift of mobile ions in the PVP layer forming a layer of electrical charge near the semiconductor interface, which subsequently changed the density of charge carriers in the semiconductor between source and drain; or, (2), ionic impurities in the PVP diffusing through the P3HT/PVP interface and directly doping the P3HT layer. In a subsequent publication, Bäcklund et al. showed that the current modulation was primarily due to the latter of these two possibilities [57], although the exact nature of the ions involved remained unclear.

Much of the data in this chapter supports the body of work already conducted by Österbacka's group on similar devices, but this chapter aims to complement and build on the existing knowledge base, and, in doing so, develop a further understanding of their current modulation mechanisms. This knowledge will also help to determine their suitability to sensing applications. The results of the experiments outlined below indicate a general agreement with the notion of electrochemical doping near the P3HT/PVP interface being the most dominant current modulation mechanism.

3.1 Performance of a Standard OTFT

An inspection of the output characteristic is an effective way of gaining a rapid assessment of transistor performance before proceeding to evaluate numerical parameters if necessary (using the methods outlined in Chapter 2). If the output characteristic shows clearly defined linear and saturation regions as well as I_D modulation with changes in V_{GS} , the device can be considered to be acting as a transistor and can be sensibly compared with other devices. Figure 3.2 shows an output characteristic of a standard OTFT showing the desired features. From $V_{DS} = 0$ V to about -0.5 V, I_D changes approximately linearly with V_{DS} (linear region) and for V_{DS} beyond -0.5 V, there is little change in I_D for changes in V_{DS} (saturation region).

Table 3.1 shows the average current modulation ratio, I_{ON} and I_{OFF} values as well as their maxima and minima over a sample of twelve standard devices fabricated at irregular intervals over a period of approximately twelve months. An average current modulation ratio of approximately 50 is similar to devices reported by Sandberg et al., who claim a figure of between 100 and 1000 [49]. Conventional FETs and pentacene-based OFETs can have current modulation ratios as high as 10^8 [15].

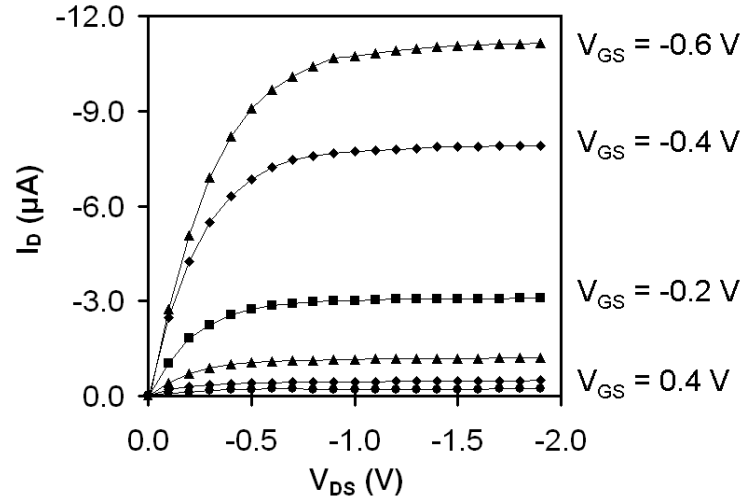


FIGURE 3.2: Output characteristic for V_{GS} between 0.4 V and -0.6 V of the “standard OTFT”.

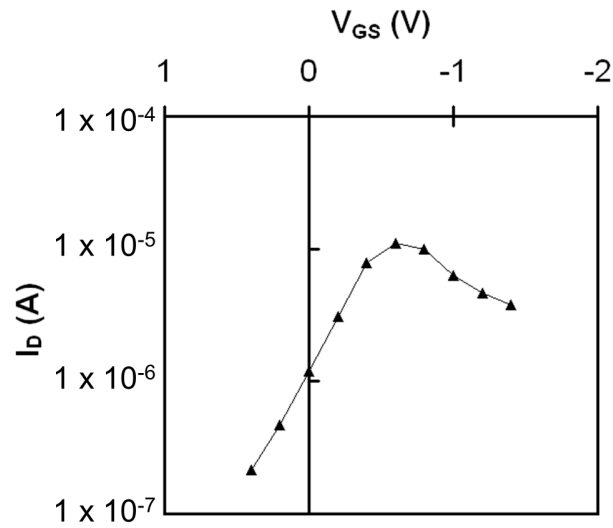


FIGURE 3.3: Standard OTFT transfer characteristic obtained from the output characteristic at $V_{DS} = -1.5\text{ V}$.

Parameter	Average $\pm \sigma$	Minimum	Maximum
I_{OFF} at $V_{DS} = -1.5$ V (A)	$7.2 \times 10^{-7} \pm 3.9 \times 10^{-7}$	4.8×10^{-8}	3.2×10^{-6}
I_{ON} at $V_{DS} = -1.5$ V (A)	$4.4 \times 10^{-5} \pm 9.8 \times 10^{-6}$	3.1×10^{-6}	3.8×10^{-4}
Current Modulation Ratio	56 ± 31	5	262

TABLE 3.1: Average ($\pm \sigma$), maximum and minimum current levels over a set of twelve standard OTFTs. Standard deviation was calculated without the maximum and minimum values for each quantity.

We can also see from Table 3.1 that there is a large variation in current levels from device to device. This variance can be explained by the fact that there are some factors relating to the fabrication process which are inherently difficult to control. For example, all devices were fabricated in air, at room temperature. Therefore, deviations in temperature and humidity, which are known to affect the characteristics of organic transistors [87–89], will result in inconsistencies in performance. In addition, one step of the fabrication process - manually drop-casting the PEDOT:PSS gate - is difficult to accurately replicate on each device. As will be discussed in Section 3.2.6, the position of the PEDOT:PSS gate has a large influence on device characteristics. In order to mitigate the inconsistencies in the characteristics of devices, data was collected from the same batch of OTFTs when controlling a certain parameter of device fabrication. This approach allows for the observation of any trends which may occur without being subject to the “noise” associated with these uncontrollable factors.

The key advantage of this type of OTFT is its low voltage operation. In the transfer curve shown in Figure 3.3, the magnitude of I_D is increased as V_{GS} becomes more negative from 0.4 V to -0.6 V, until a decrease in current can be seen when V_{GS} is switched from -0.6 V to -0.8 V and lower. The value of V_{GS} which induces the highest I_D whilst maintaining transistor-like behaviour changes from device to device but is usually in the range of -0.6 V to -1.0 V. The devices switch from “off” to “on” with a change in V_{GS} of about 1 V which is very low voltage operation compared with the majority of OTFTs (particularly OFETs) which operate at much higher voltages, often requiring several tens of volts to turn on [15, 90].

Figure 3.4 shows a transfer curve measured in both “directions” of V_{GS} (positive to negative and vice versa) at $V_{DS} = -1.5$ V, with a 1 s interval between changes in V_{GS} . The current levels (I_{ON} and I_{OFF}) are similar to those of the transfer curve plotted from data measured during the output characterisation (Figure 3.2), however there is little (if any) hysteresis between the two directions.

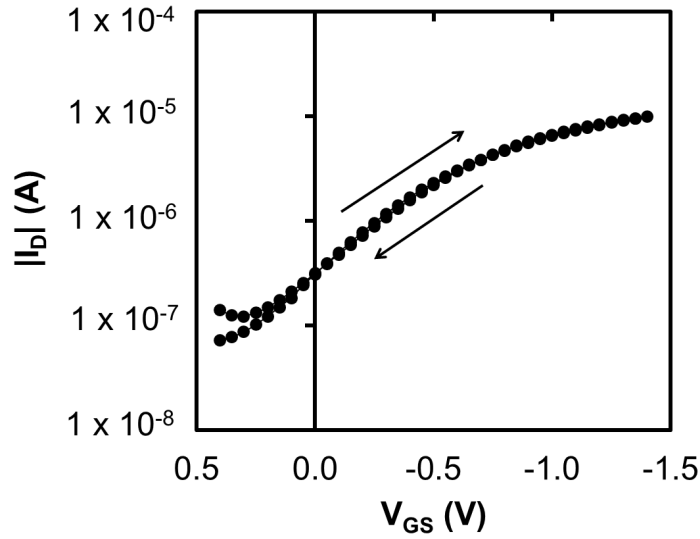


FIGURE 3.4: Standard OTFT transfer characteristic measured directly with $V_{DS} = -1.5$ V.

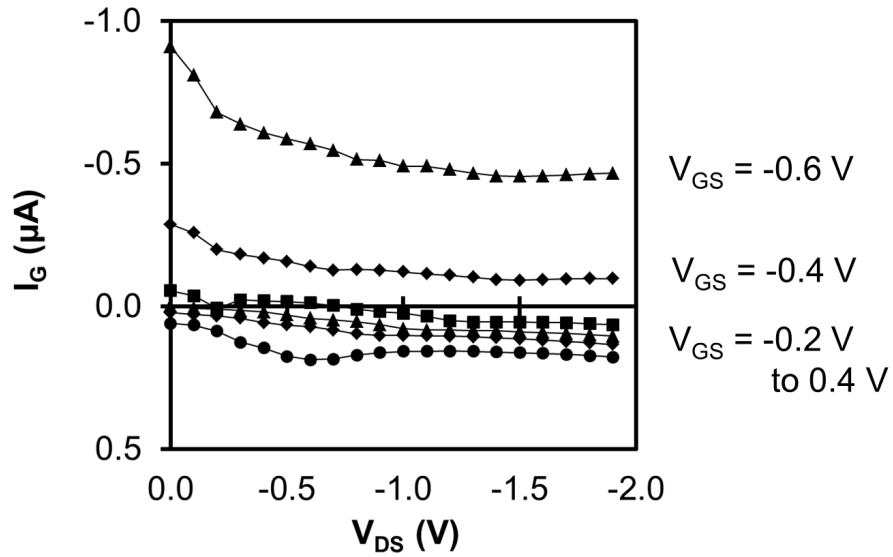


FIGURE 3.5: Standard OTFT gate leakage currents.

Figure 3.5 shows the leakage currents for the same range of V_{GS} for which the output characteristic in Figure 3.2 was measured. When the device is “on” (at $V_{GS} = -0.6$ V), I_G is more than an order of magnitude lower than the corresponding I_D values meaning that a relatively low amount of current flowing in the devices comes from the gate, thus meeting a desired requirement of OTFTs as mentioned in Chapter 1.

3.2 Studies to Determine the Mechanisms Involved in Current Modulation

In order to probe the mechanisms involved in the operation of these OTFTs, a variety of experiments involving variations to the fabrication procedure or using different measurement techniques were conducted and are reported in this section. The discussions and conclusions drawn from these experiments are also summarised.

Previous work investigating the mechanism of current modulation in these devices has shown that H^+ and OH^- ions are mobile within the dielectric layer and drift according to the voltages at the electrode and subsequently dope and de-dope the semiconductor layer, causing increases and decreases in its conductivity [27, 48, 49, 57, 84, 85]. This hypothesis will be assessed based on the results presented here.

3.2.1 P3HT Thickness Study

In this section, the thickness of the P3HT layer in the OTFTs was controlled, the associated changes in output characteristics observed and the results discussed. To date, no such study has been conducted on OTFTs of this type.

Previous work by Bäcklund et al. (Österbacka’s group) [57] has shown that current modulation in these types of OTFT devices is governed by electrochemical doping of the P3HT semiconductor layer. However, it is unclear whether this doping affects the bulk of the P3HT layer, or just the P3HT/PVP interfacial region. Studying the impact of semiconductor layer thickness on device behaviour is one way to determine the proportion of the P3HT layer which is influenced. If there is bulk-doping of the P3HT layer occurring, increasing the thickness would provide an opportunity for a larger cross-section of polymer between source and drain to be doped, and hence induce higher I_{ON} values. On the other hand, reducing the P3HT thickness would mean a lower conductivity between source and drain.

If, however, the current modulation mechanism is based around activity at the semiconductor-dielectric interface, increasing the P3HT thickness would potentially decrease I_{ON} . In conducting polymers, charge transport more readily occurs along the long polymer “backbones” than it does between polymer chains [42]. The thicker

P3HT Concentration (mg/ml)	Average Thickness $\pm \sigma$ (nm)
5	25 ± 8
10	59 ± 18
20	144 ± 34
40	447 ± 81

TABLE 3.2: Average P3HT film thicknesses and standard deviations for films spun from different concentrations in chloroform.

the P3HT film, the larger the distance between the source and drain electrodes and the semiconductor-dielectric interface, and the further charge carriers must travel in a direction perpendicular to the polymer backbones to reach the interface. Figure 3.6 shows the difference between where bulk and interface doping could occur in the devices.

The thickness of the P3HT layer was varied by changing the concentration of polymer in the chloroform solution when spin-coating that layer. Solutions of 2 mg/mL, 5 mg/mL, 10 mg/mL, 20 mg/mL and 40 mg/mL of P3HT in chloroform were used, where 20 mg/mL is the concentration used in a standard device. Aside from the P3HT concentration, the other fabrication steps remained as described in Chapter 2. The thickness of these films was measured by profilometry on films spun onto glass slides from the same solutions used to make the transistors. Table 3.2 shows a summary of the film thicknesses by polymer concentration. Films spun from 2 mg/mL concentration of P3HT in chloroform were too thin to be accurately measured using profilometry.

Devices fabricated from the 2 mg/mL solution did not show an output characteristic comparable to the other devices. Firstly, for $V_{DS} > 0.8$ V, there was no “turn on” observed in I_D , and although the characteristic observed for $V_{DS} < 0.8$ V showed some modulation with V_{GS} , there were higher than expected leakage currents ($|I_G| > 100 \mu\text{A}$) possibly indicating that the PEDOT:PSS has caused a short to the source and drain electrodes due to the thin P3HT layer being discontinuous. Films spun from the other (higher) concentrations all produced devices with transistor-like behaviour (Figure 3.7). As such, it is clear that 2 mg/mL is below the critical concentration needed to form working semiconductor layers in the devices.

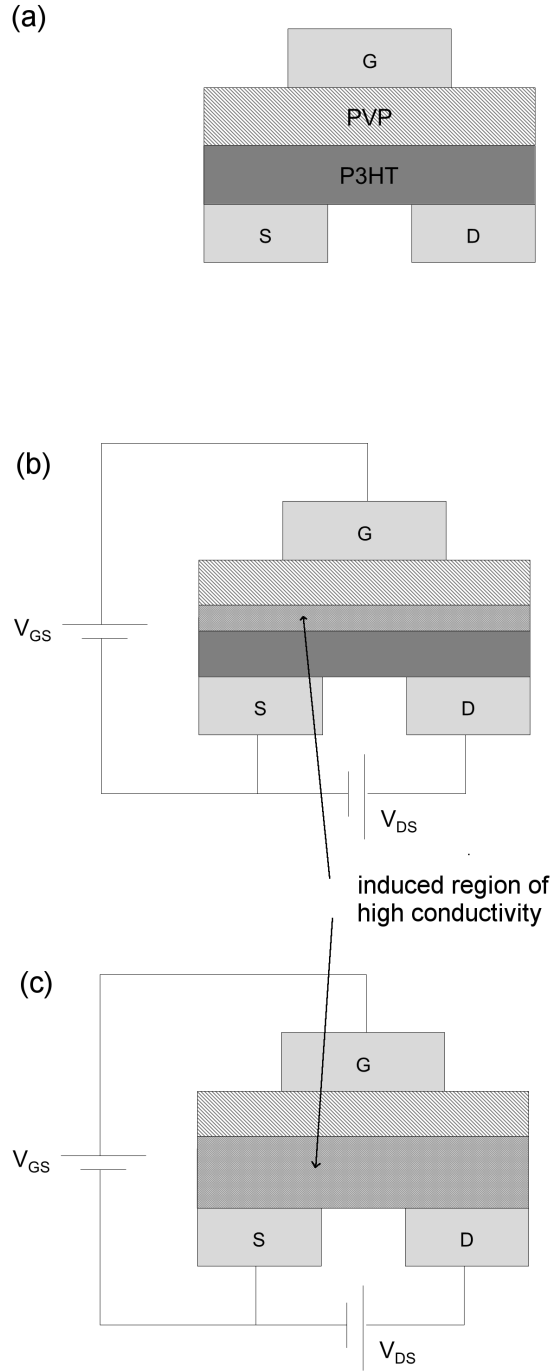
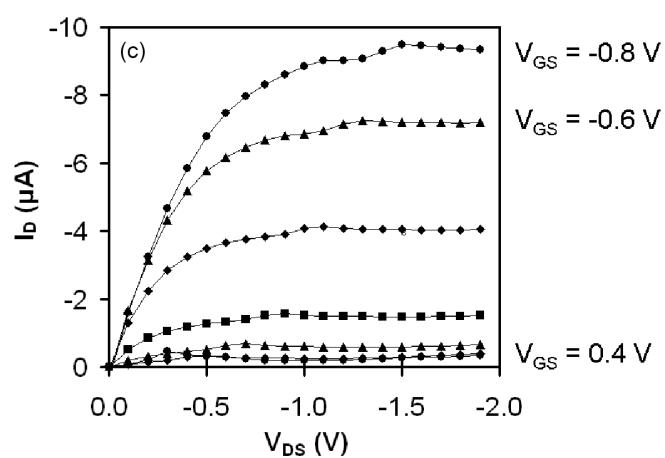
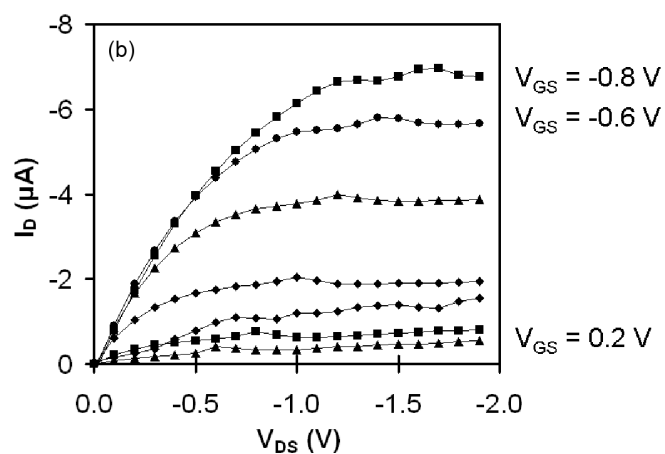
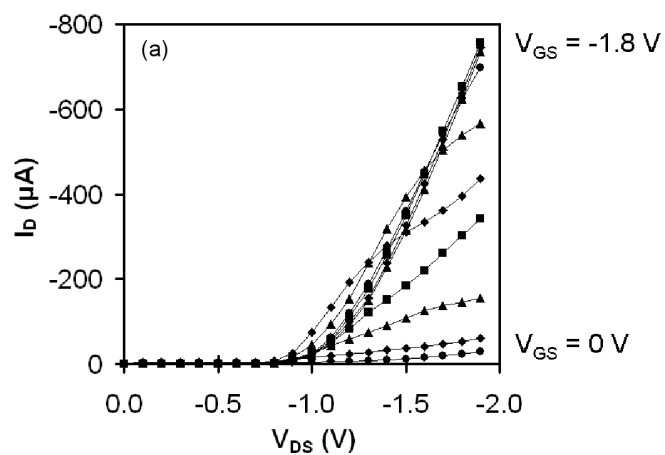


FIGURE 3.6: Cross-sectional diagram of the standard OTFT showing: (a) the device with no voltage source connected; (b) the device biased to conduct I_{ON} as viewed if interfacial doping is occurring; and, (c), the device biased to conduct I_{ON} as viewed if bulk doping is occurring.



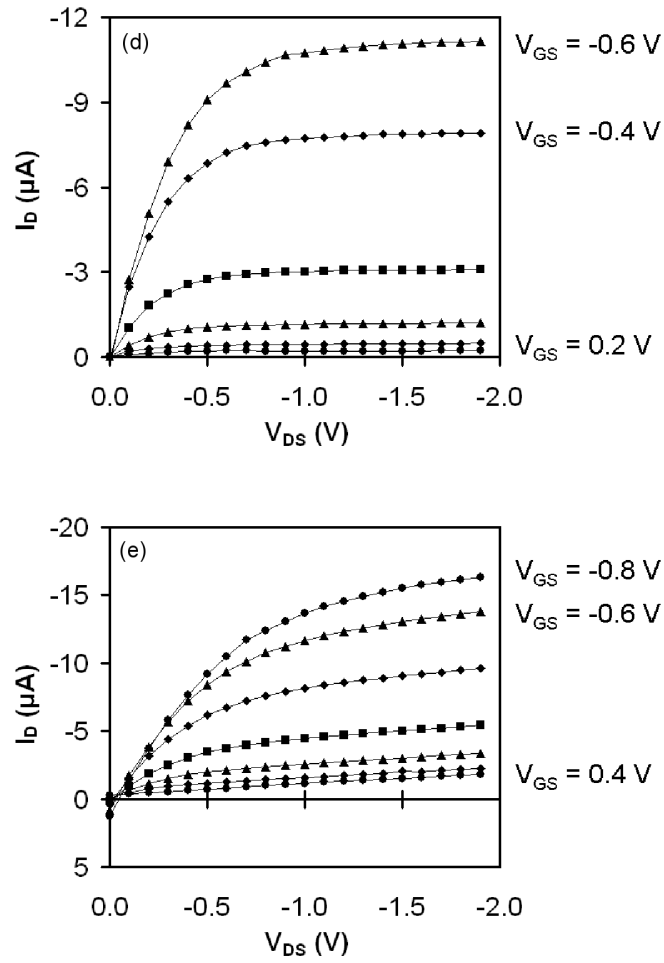
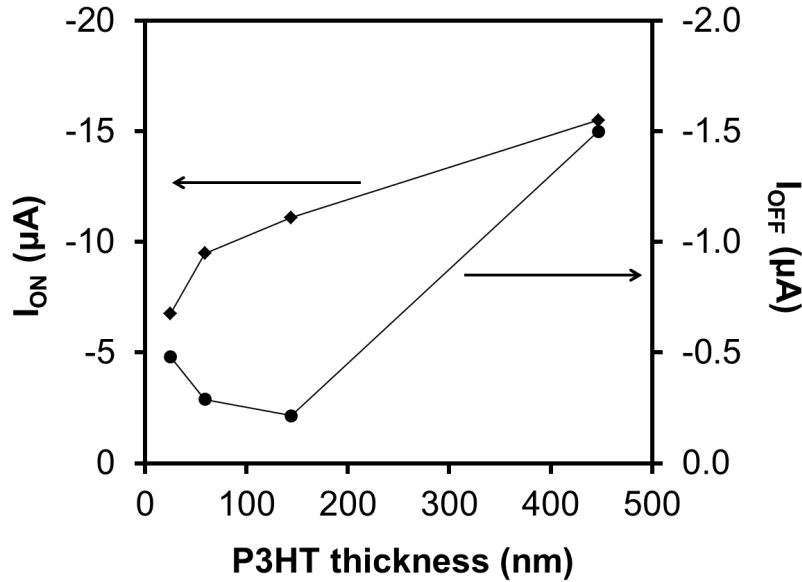


FIGURE 3.7: Output characteristics of OTFTs employing semiconducting films made from different concentrations of P3HT in chloroform: (a) 2 mg/mL (incomplete coverage), (b) 5 mg/mL (average thickness = 25 nm), (c) 10 mg/mL (average thickness = 59 nm), (d) 20 mg/mL (average thickness = 144 nm), and (e) 40 mg/mL (average thickness = 447 nm).

Average P3HT Thickness (nm)	I_{OFF} (A) at $V_{DS} = -1.5$ V	I_{ON} (A) at $V_{DS} = -1.5$ V (A)	Current Modulation Ratio
25 (5 mg/mL)	-4.8×10^{-7}	-6.8×10^{-6}	14
59 (10 mg/mL)	-2.9×10^{-7}	-9.5×10^{-6}	33
144 (20 mg/mL)	-2.1×10^{-7}	-1.1×10^{-5}	52
477 (40 mg/mL)	-1.5×10^{-6}	-1.6×10^{-5}	11

TABLE 3.3: Current levels of OTFTs with different P3HT thicknesses.

FIGURE 3.8: I_{ON} and I_{OFF} versus P3HT thickness.

The output characteristics shown in Figure 3.7(a) through Figure 3.7(e) all show I_{ON} , I_{OFF} and current modulation ratio values within the range of values for standard devices given earlier in Table 3.1, meaning that all of the current values could be considered to be within error. However, as mentioned earlier, variations in devices can largely be attributed to temperature and humidity variations (an idea introduced in Section 3.1). To ensure consistent behaviour, all devices for this study were fabricated on the same day under the same conditions and as such any trends which are observed are likely to be due to the controlled variations in P3HT thickness.

The PEDOT:PSS suspension which forms the gate electrode is highly acidic [76], and hence a rich source of protons. This contribution of protons can conceivably affect

the devices in two different ways. Firstly, the P3HT layer could be doped by these protons upon deposition, which would result in an increase in the P3HT's base conductivity, and hence increase the minimum potential I_{OFF} value. This increase in I_{OFF} would lower the maximum possible current modulation ratio, thereby diminishing device performance. Secondly, it has been postulated previously by Bäcklund et al. [57] that H^+ contributes to the ionic current modulation mechanisms in the devices. As such, the protonic contribution from the PEDOT:PSS could possibly act to enhance current modulation.

Table 3.3 and Figure 3.8 show that although there is an increase in I_{ON} with P3HT thickness, the device with the thickest layer also has by far the highest I_{OFF} value, meaning that its current modulation ratio is lower than the other devices. However, in the case of the devices with the three lowest thicknesses, there is a decrease in I_{OFF} with increasing P3HT thickness. It is conceivable that this trend is due to the thinner layers being relatively more doped (prior to any mechanisms induced by a gate potential) by the protons in the acidic PEDOT:PSS solution, in turn forming a conductive pathway between gate and the source/drain electrodes, which is supported by an associated decrease in these devices in I_G in the “off” state ($V_{DS} = -1.5$ V and $V_{GS} = 0$ V). Also, in each case the increase in I_{ON} compared with next thinnest device is less than 50 %, despite the more than 200 % increase in P3HT thickness from one thickness to the next. This result indicates that P3HT is mainly doped close to the dielectric interface and less so in the deeper regions of the semiconductor. If “bulk-doping” was occurring, devices would be expected exhibit proportional increase in I_{ON} with P3HT thickness.

3.2.2 PVP Thickness Study

The effect on devices of changing PVP thickness was studied previously by Österbacka's group [57]. However, only two thicknesses were considered, and the changes in the output characteristics of devices made with the two different thicknesses were seen to be insignificant. This conclusion leaves un-answered the questions: (a) what significance the dielectric thickness has on device performance, and, (b) whether or not there is an optimum PVP thickness.

If the ions involved in current modulation indeed originate predominantly from the PVP film attracting water, it is expected that the current modulation ratio in a device with a thicker PVP layer could be higher than a standard device. This prediction comes from the idea that there would be more ions available to contribute to the current modulation mechanism regardless of which of the two mechanisms suggested by Österbacka's group is occurring (drift, or diffusion/doping). On the other hand, if these ions are contributed mainly by the PEDOT:PSS solution of the gate electrode, a thicker dielectric layer would inhibit the progress of ions to the semiconducting layer thereby resulting in lower current modulation and/or lower I_{OFF} values or increasing the operating voltage required at the gate to turn the devices on (i.e. a higher value of $|V_{TH}|$).

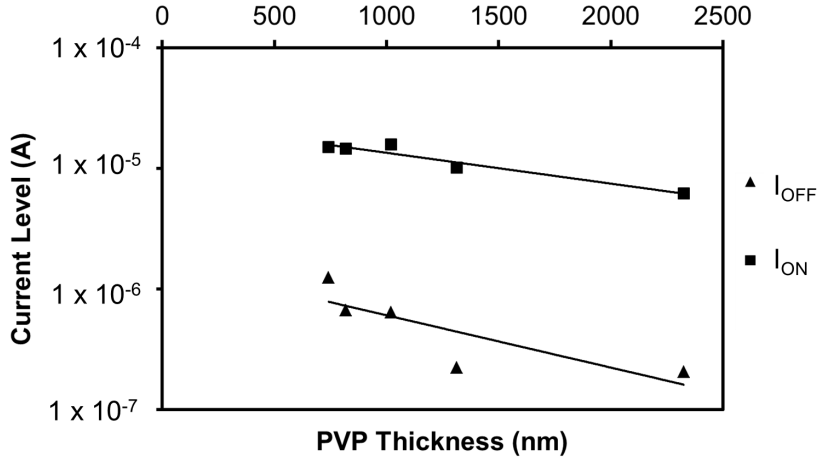


FIGURE 3.9: PVP thickness investigation - batch 1.

To probe the role of PVP in the device, an investigation was conducted whereby the thickness of the PVP layer was controlled and the output characteristics of the associated devices compared. The thickness was controlled both by varying the concentration of PVP in ethanol as well as varying the speed of the spin-coater. PVP solutions in ethanol of concentrations of 40 mg/mL, 60 mg/mL, 80 mg/mL, 120 mg/mL and 160 mg/mL were prepared, where 80 mg/mL is used in the standard devices. However, attempts to spin films from concentrations of 40 and 60 mg/mL were unsuccessful. Hence, PVP films spun from concentrations lower than normal were not able to be produced. Spin speeds used were 1000, 2000 and 4000 rpm. See Table 3.4 for the thicknesses of the films produced.

The trend in both cases shown in Figure 3.9 and Figure 3.10 is that levels of both I_{ON} and I_{OFF} tend to fall with increasing PVP thickness. This observation aligns with that of Bäcklund et al., who also observed a decrease in I_D in HIFETs (which had gold source, drain and gate electrodes - no PEDOT:PSS gate) when the PVP thickness was changed from 900 nm to 2400 nm [57]. There are two possible explanations for the observed trends. The first hypothesis is that the PVP layer simply acts as a physical barrier between the P3HT active layer and any protonic contribution to the P3HT layer from the PEDOT:PSS solution when it is drop-cast as the gate is inhibited by the PVP. The thinner the PVP layer, the more likely it is for PEDOT:PSS to make direct contact with the P3HT layer upon deposition by filling any cavities in the dielectric layer. If this contact occurred, the PEDOT:PSS could dope the P3HT layer due to its abundance of protons. With thicker PVP layers, contact is less likely to occur and thus I_{ON} and I_{OFF} would be lower. An alternative explanation is simply that the

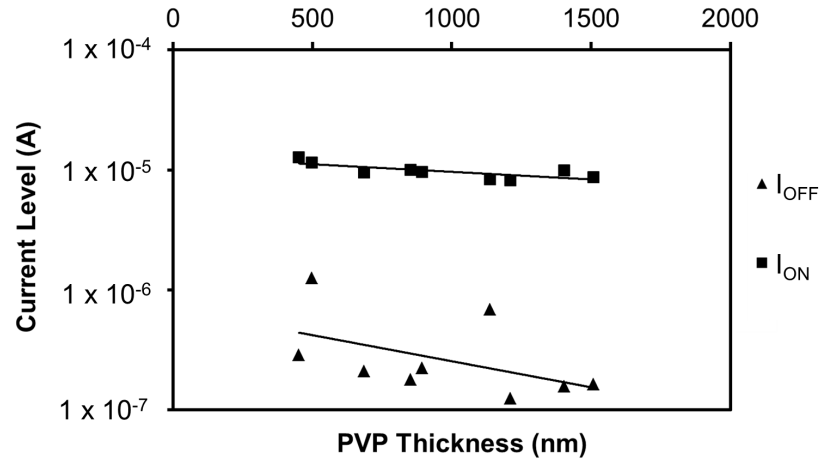


FIGURE 3.10: PVP thickness investigation - batch 2.

PVP Concentration (mg/mL)	Spin Speed (rpm)	Average Thickness Batch 1 (nm)	Average Thickness Batch 2 (nm)
80	1000	-	686
80	2000	488	498
80	4000	-	451
120	1000	-	1211
120	2000	741	893
120	4000	817	851
160	1000	2324	1508
160	2000	1306	1404
160	4000	1019	1136

TABLE 3.4: PVP film thicknesses for films spun from different concentrations at different speeds.

thicker dielectric layer means that any layers of charge established at the P3HT/PVP interface would be weaker for thicker PVP layers due to the distance between the PEDOT:PSS gate at this interface. This weaker electrostatic mechanism would result in lower induced I_{ON} values. Note that the physical blocking mechanism and the ionic, electrostatic mechanism are not mutually exclusive and could potentially both be occurring simultaneously.

3.2.3 Characterisation in “Wet” and “Dry” Environments

If ionic movement within the PVP dielectric layer is a large contributor to the current modulation mechanisms in these standard devices, it follows that removing ions from the device would affect their transistor characteristics to some degree.

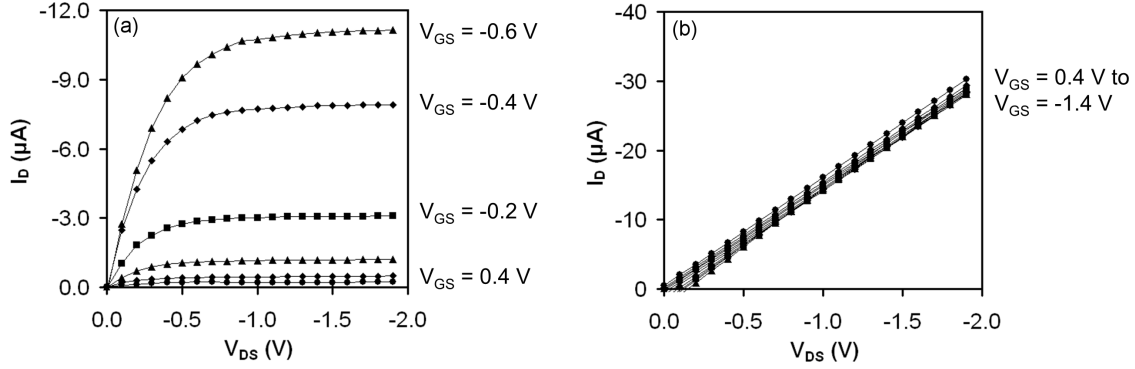


FIGURE 3.11: Standard OTFT output characteristic measured (a) in air (normal measurement conditions); and (b), in a nitrogen-rich glove box.

Previous work by Österbacka's group investigating the origin of ions in the devices has argued that there are H^+ and OH^- ions liberated from the presence of water in the device [27]. PVP, being a highly hygroscopic material [27, 49], tends to attract water from its surrounds. By characterising devices in air and also in a humidity-free, nitrogen-rich environment, their response can be expected to be significantly different if the atmosphere in which the device is measured contributes significantly to device performance.

In this section, devices are characterised in and out of a dry nitrogen environment to see if current modulation can be lost and restored multiple times. Furthermore, the current level of devices when measured in the dry atmosphere is compared with that when measured in air. Standard OTFTs were fabricated: some were characterised in air and the others in a nitrogen-filled glove box after being allowed to equilibrate for approximately 72 hours. Some devices which were tested first in air were then subsequently tested in the glove box and vice versa, to determine if the influence of atmosphere extended beyond the initial measurement, since, when testing in air, it has been observed that the output characteristic of a device changes significantly after the first measurement (see Section 3.2.4).

Figure 3.11(b) shows the output characteristic of a standard OTFT measured for the first time in the glove box after equilibration and shows that there is very little current modulation occurring within the range of gate voltages usually used for characterising the devices in air (V_{GS} between 0.4 to -1.4 V). Furthermore, there is no saturation region in the output characteristic - it behaves linearly over the extent of the tested voltages. Therefore, we can say that whatever mechanism leads to current modulation is now not operating in the device. Figure 3.11(a) is the output characteristic of a standard device measured in air and is provided for comparison.

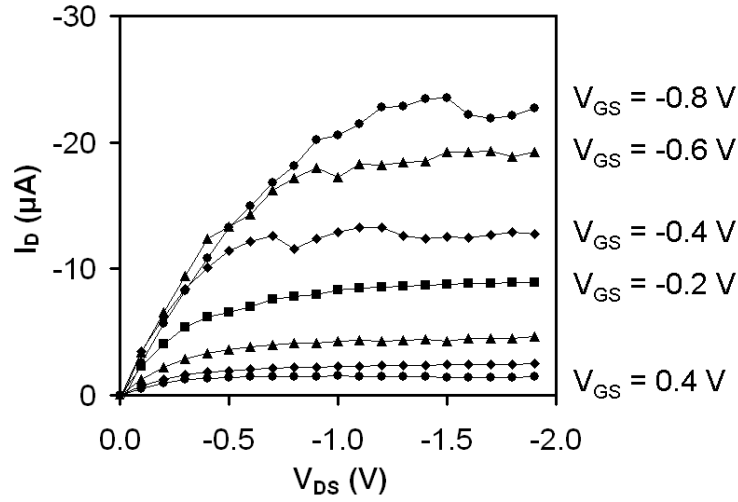


FIGURE 3.12: Standard OTFT output characteristic measured in air after being measured in the glove box (same device as Figure 3.11).

Figure 3.12 shows the output characteristic of the same device measured in Figure 3.11, this time measured in air after being out of the glove box for several days. Clearly, an output characteristic which closely resembles the standard OTFT output characteristic has been restored, indicating that air exposure reactivates the current modulation mechanism.

Figure 3.13 shows a series of transfer curves from a standard device which was first tested in the glove box, secondly in air, then in the glove box again and finally in air. The transfer curves were obtained from the output characteristics at $V_{DS} = -1.5$ V. Figure 3.13 clearly shows the restoration and loss of current modulation as the device is removed from, and replaced in the nitrogen-rich, low-humidity glove box. In the case of the fourth measurement (the second measurement in air), there is some restoration in current modulation for the device, but it is reduced in comparison to the first characterisation in air. This reduction is consistent with observations made upon repeated scanning of devices in air (Section 3.2.4), confirming the fact that measuring devices in air causes a degradation in their current modulation capability.

Figure 3.14 shows transfer characteristics for a device measured firstly in air and then in the glove box, and verifies that the process can be conducted in reverse - that is, current modulation can also be recovered when the initial characterisation is conducted in the dry environment. However, the level of I_D when measured in the glove box is more than one order of magnitude lower than those devices which were initially measured there. This reduction in I_D could possibly due to over-oxidation of the P3HT

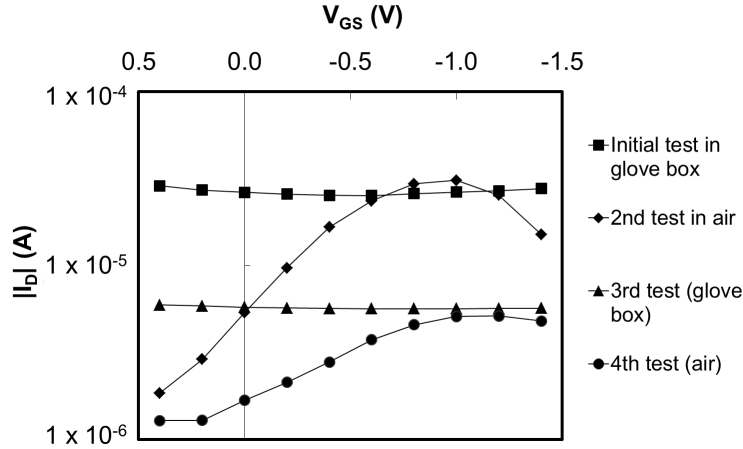


FIGURE 3.13: Transfer characteristics (obtained from output characteristics) of a device measured firstly in the glove box, then in air, then thirdly in the glove box and finally in air).

layer, which is discussed further in Section 3.3.

Sandberg et al. have previously shown that current modulation in their P3HT and PVP-based “HIFETs” is prevented when testing is conducted in a dry nitrogen environment, both with a PEDOT:PSS gate and with a gold gate [27, 49]. Since it is likely that the acidic PEDOT:PSS solution is contributing ions to the dielectric of a standard OTFT, we can say that any contribution to current modulation from the PEDOT:PSS gate can be removed from the device in exactly the same way that the effect from the hygroscopic dielectric can, since in both cases there is no modulation in the dry environment. This observation is a strong indicator that H^+ ions are involved in the devices’ operation since the PEDOT:PSS suspension is highly acidic and thus will be a source of H^+ ions.

Intuitively, it may seem that modulating the I_D levels in the transistor (when measuring in air) involves inducing a region which has a higher conductivity than the “base” conductivity level of the semiconductor, thereby increasing current levels from some base level. However, in the glove box, where no current modulation is observed, the I_D levels are high compared with the I_{OFF} values from measurements conducted in air. Moreover, at $V_{GS} = 0$ V the initial slope (for V_{DS} between 0 V and -0.1 V) of the output curve seems to be approximately the same in both cases, however in the case of the measurement taken in air, I_D saturates to a level lower than that observed in the glove box (Figure 3.15). Also, by looking at the transfer curves from the first two measurements in Figure 3.13, the I_{ON} level observed when characterising in air is approximately the same as I_D for all V_{GS} values in the glove box (as noted above V_{GS} does not modulate I_D in the dry glove box environment). This observation indicates that the modulation of I_D in a humid atmosphere (e.g. air) being due to *de*-doping of a base

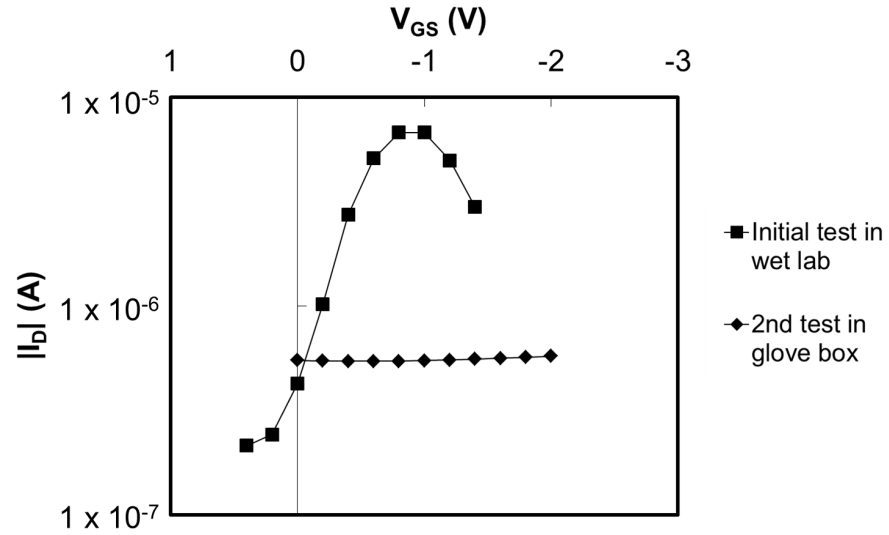


FIGURE 3.14: Transfer characteristics (obtained from output characteristics) of a device measured firstly in air, then in the glove box.

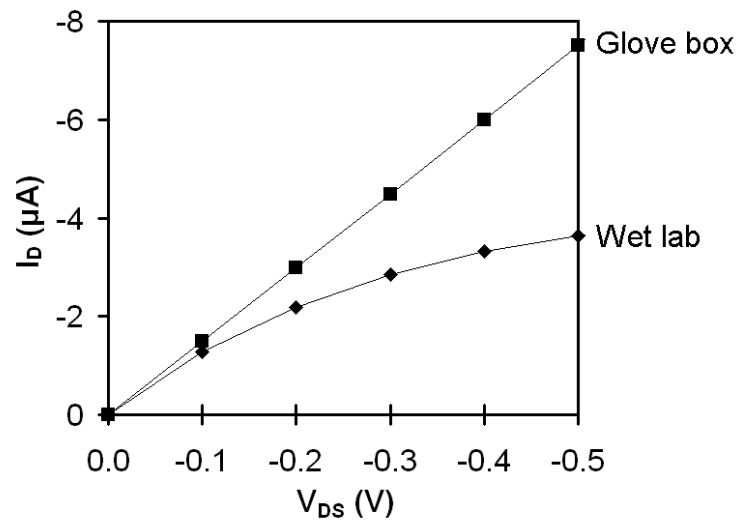


FIGURE 3.15: Comparison of the same OTFT measured in the glove box and then in air at $V_{GS} = 0$ V.

level of semiconductor conductivity rather than the doping of a base conductivity state.

3.2.4 Repeated Characterisation and Gate Voltage Effects

In measuring the output characteristic of a standard OTFT, once the device has been measured once, a systematic change in the characteristic in subsequent measurements is observed. Upon repeated measurement, the devices exhibit reduced current modulation and degraded saturation regions. This degradation can be seen in the transfer curves taken from the repeated measuring of a device shown in Figure 3.16(a). The second scan shows significantly less current modulation than the first, while the third and forth measurements show almost no current modulation at all.

When characterising OTFTs, the gate voltage is typically swept from $V_{GS} = 0$ V or $V_{GS} = 0.4$ V to $V_{GS} = -1.4$ V or $V_{GS} = -2$ V. If the degradation in the output characteristics of device on measurements subsequent to their first is due to an electrochemical change in the device, it seems reasonable to speculate that this may take place at a certain value of V_{GS} . As such, if the gate voltage is restricted to below a certain threshold, it may be possible to achieve highly repeatable transfer characteristics without this decaying response.

An experiment was conducted to attempt to determine if there was a threshold value of V_{GS} which induced this reduction in I_D levels. The range of V_{GS} which was applied to the device was gradually increased over a sequence of characterisation measurements. The drain voltage was scanned from $V_{DS} = 0$ V to -2 V in each case, and the transfer characteristics presented are for $V_{DS} = -1.5$ V.

As can be seen from the transfer curves shown in Figure 3.16(b) there is little to no change in the transfer characteristic in the first three measurements, each of which were taken between $V_{GS} = 0.4$ V and -0.4 V. The fourth scan, which is taken from $V_{GS} = 0.4$ V to -0.6 V follows the same “path” as the first three between $V_{GS} = 0.4$ V and -0.4 V. The fifth scan, however, taken between $V_{GS} = 0.4$ V to -0.8 V shows a clear shift in the transfer characteristic towards lower I_D levels, indicating that an electrochemical (or other) change may be taking place in the device at some threshold value of V_{GS} between -0.4 V and -0.6 V causing degradation in the P3HT conductivity.

The notion that the degradation of the I_D levels in the devices (occurring once a certain threshold of V_{GS} has been exceeded) is due to an electrochemical change in the P3HT is supported by previous research on the electrochemical properties of P3HT. Ulgut et al. conducted cyclic voltammetry on P3HT films cast onto the working electrode of a three-terminal electrochemical cell [91]. The results of their experiments indicated oxidation and reduction peaks occurring at working electrode potentials (V_{WE}) of between 550 mV and 650 mV relative to the reference electrode. In the case of the OTFTs being studied here, the gate electrode would be acting similarly to the reference

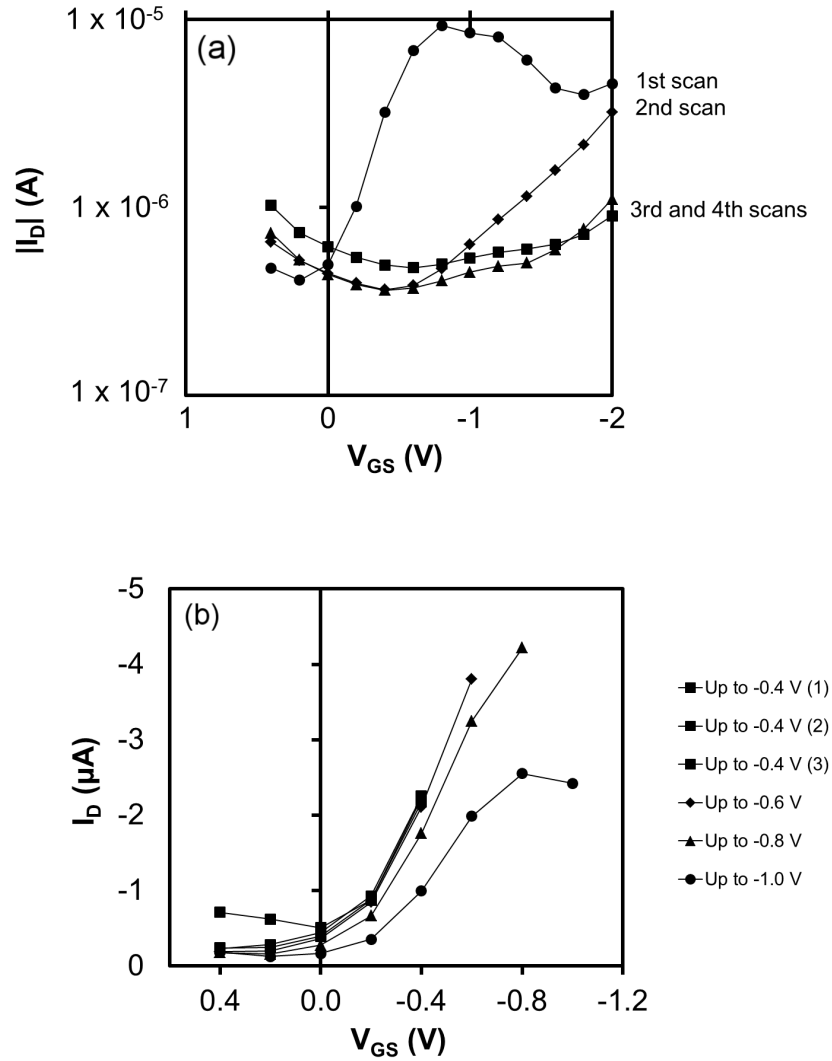


FIGURE 3.16: Transfer characteristics (obtained from output characteristic measurements at $V_{DS} = -1.5$ V) of standard OTFTs under repeated measurement: (a) with V_{GS} taken from 0.4 V to -2 V each time, and (b) with the range of V_{GS} starting at 0.4 V to -0.4 V and increasing in the negative direction after three scans at the initial range (shown on a linear graph to accentuate the changes in I_D).

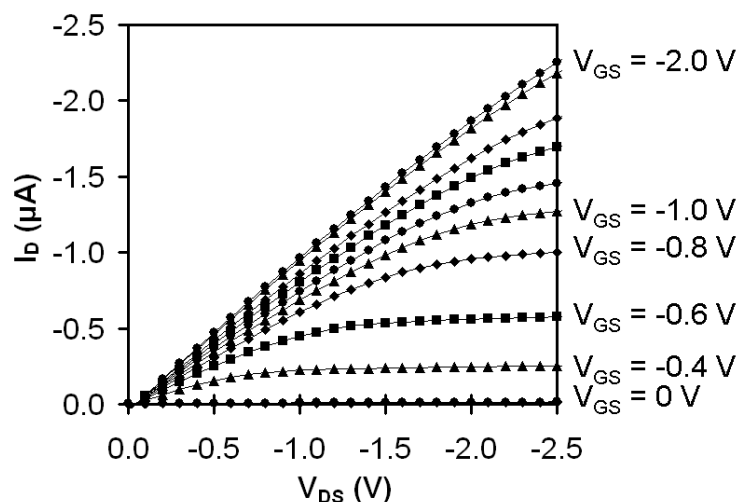


FIGURE 3.17: Output characteristic of an OTFT with an aluminium gate.

electrode of the electrochemical cell and the drain or source potentials (relative to the gate) are equivalent to V_{WE} . The fact that the shift in device characteristic is observed to occur for $V_{GS} < -0.6$ V (equivalent to $V_{WE} > 0.6$ V, and close to the reported redox potentials) makes the reason for the change likely due to oxidation or reduction of the P3HT layer.

3.2.5 Aluminium Gate Electrode

In order to further determine the contribution of the PEDOT:PSS gate, devices were constructed using an aluminium gate (deposited by thermal evaporation) and the characteristics were observed. The output characteristic of one of these devices is shown in Figure 3.17. Although a device with a transistor-like response has been fabricated, without the PEDOT:PSS being added to the device, the I_{OFF} levels are very low at approximately 1×10^{-8} A. Furthermore, the I_{ON} at $V_{GS} = -1$ V and $V_{DS} = -2$ V is 1.5×10^{-6} A, giving a current modulation ratio of about 150, superior to most standard OTFTs. Clearly, the addition of PEDOT:PSS as a gate contributes to the high I_{OFF} of the standard devices. Although the aluminium evaporation step necessarily requires the devices to be exposed to vacuum, and therefore having their moisture levels reduced, the devices were allowed to equilibrate in air prior to characterisation so it is assuming here that the hygroscopic PVP layer has been allowed to fully hydrate before the output characteristic measurements were taken. This hypothesis is supported by the fact that PVP can attract the ions needed to facilitate current modulation after a device has been dried out, as suggested by the studies presented in Section 3.2.3.

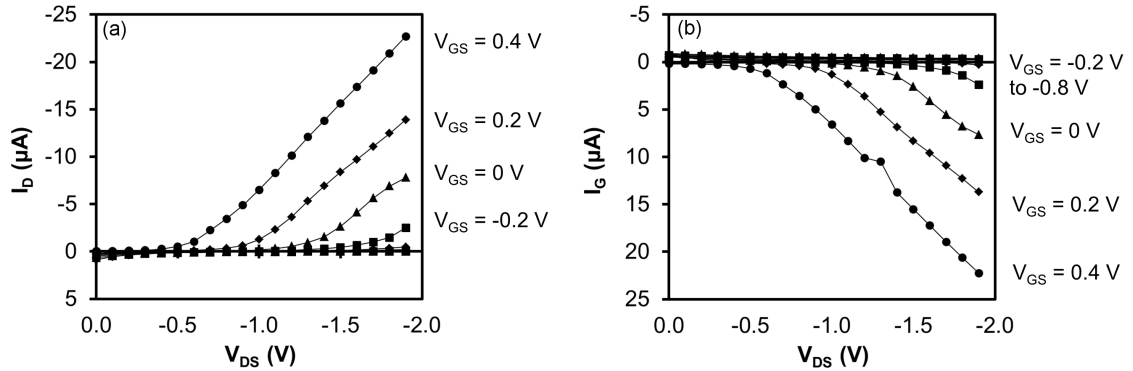


FIGURE 3.18: Characteristics of a OTFT-like construct made with no P3HT semiconducting layer: (a) output characteristics, and (b), leakage currents.

Note that the step of adding an aluminium gate, whilst creating a relatively high-performance device, is not in line with the aim of fabricating all-polymer OTFTs using simple, low-temperature processes in air. As such, this is not considered to be a way to potentially improve the standard devices, rather it was conducted to observe the device characteristics when PEDOT:PSS was not present.

3.2.6 PEDOT:PSS Gate Position Study

In the fabrication procedure of the standard devices, the step with the greatest propensity to variation is the drop-cast PEDOT:PSS gate layer. In Section 3.2.2, data was presented suggesting that thicker PVP layers inhibit the amount by which the PEDOT:PSS gate dopes the P3HT layer upon deposition. In other words, it has been shown that the highly conductive PEDOT:PSS diffuses through the PVP layer to some degree. When the gate electrode is deposited in a standard device, care is taken to ensure that it is fully contained within the outline of the patterned P3HT layer (other than the connection to the ITO pad). If the gate is offset such that it overlaps an area of either the source or drain not covered by P3HT, it is anticipated that the electrical characteristics will be changed due to lower resistance between the gate and the other electrode(s). A short study was conducted to determine the change in output characteristic as a function of gate position.

Initially, a construct was fabricated with the same structure as the standard OTFT, however the P3HT semiconductor layer was omitted, and its electrical characteristics measured. This experiment was designed to exaggerate the effect on a device in which the PEDOT:PSS is not inhibited by the P3HT to contact with the source and drain electrodes. Figure 3.18(a) shows the output characteristic of the construct with no P3HT. The traces on the output characteristic appear to have a diode-like response,

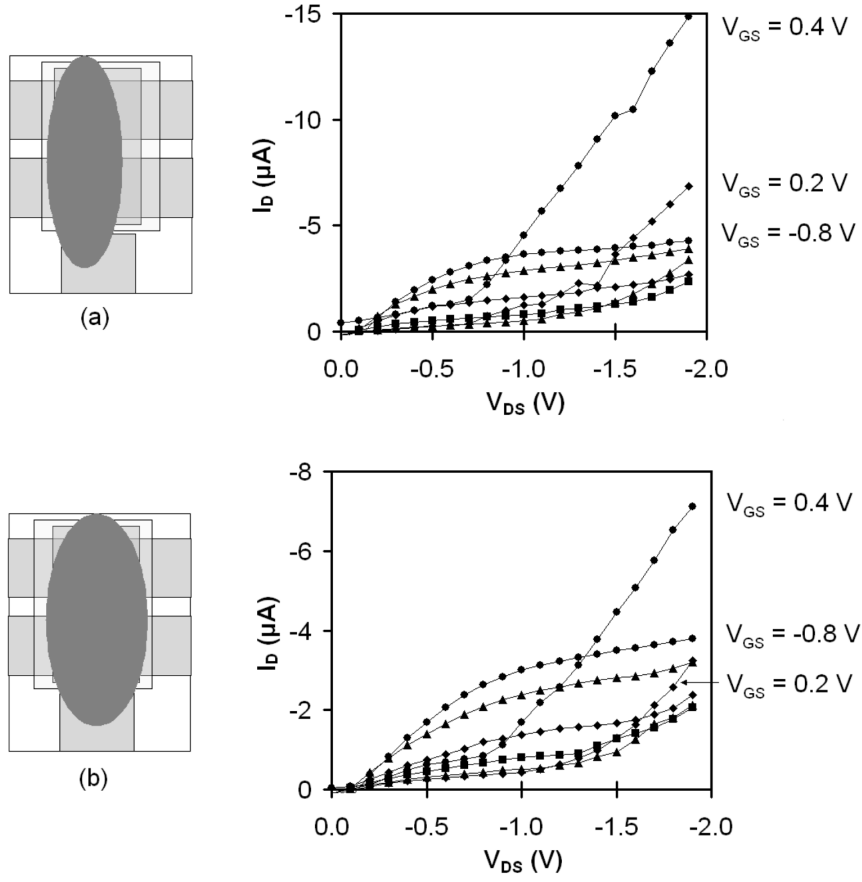


FIGURE 3.19: Illustration of PEDOT:PSS gate positions in this investigation along with their associated output characteristics: (a) Standard device structure with PEDOT:PSS gate offset on one side only, (b) Standard device structure with PEDOT:PSS gate offset on both sides.

with the I_D levels decreasing for more negative values of V_{GS} - the opposite relationship to that observed for the standard transistor. The suspected increased contribution to device behaviour from gate leakage is confirmed by Figure 3.18(b) which shows that I_G is almost a mirror image of I_D for the same V_{DS} and V_{GS} (with the polarity reversed). In other words, most of the current in the system is flowing between drain and gate.

Next, standard devices were fabricated with their gate electrodes intentionally deposited such that they lay partially outside the outline of the patterned P3HT. Two different variations in position of the gate were used: (1) the gate overlapping the exposed PVP layer on one side only (Figure 3.19(a)) and, (2) the P3HT layer overlapping the PVP layer on both sides (Figure 3.19(b)).

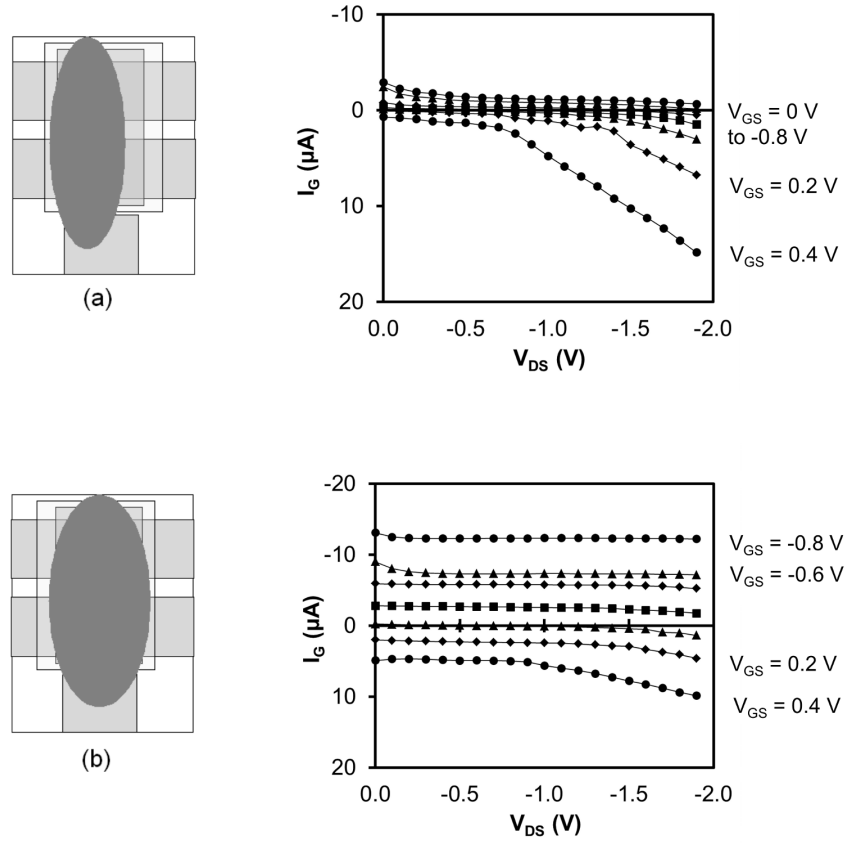


FIGURE 3.20: Illustration of PEDOT:PSS gate positions in this investigation along with their associated leakage currents: (a) Standard device structure with PEDOT:PSS gate offset on one side only, (b) Standard device structure with PEDOT:PSS gate offset on both sides.

As can be seen from a qualitative assessment of the output characteristics in Figure 3.19(a) and Figure 3.19(b), both devices with PEDOT:PSS overlapping the PVP layer show some typical OTFT output behaviour, seemingly superimposed with the behaviour of a device made without a P3HT layer (Figure 3.18(a)). The latter exhibits no transistor-style current modulation but at low, positive V_{GS} values shows a diode-like response. Thus, there is some current flowing though the PEDOT:PSS diffused through the PVP layer and making an electrical connection to the source, the drain or both.

Figure 3.20 shows the gate leakage characteristics (I_G versus V_{DS}) for the two offset-gate devices: (a) offset one side, and (b), offset both sides. Figure 3.20(a) is similar in appearance to Figure 3.18(b), the leakage characteristic for the thin film structure made with no P3HT layer. This similarity implies an electrical connection

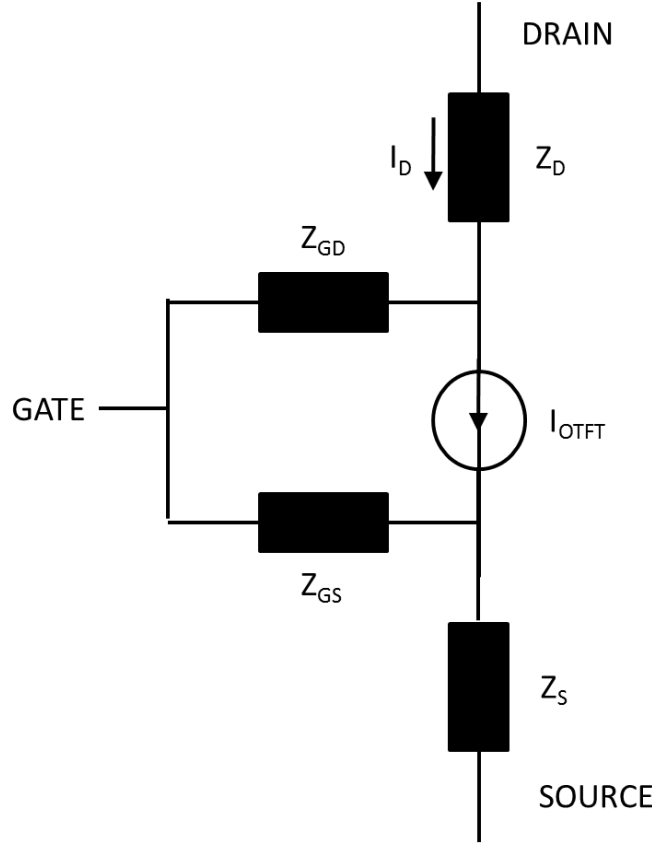


FIGURE 3.21: Simple equivalent circuit for the standard OTFT.

between gate and drain as suspected. For Figure 3.20(b), there is some similarity to Figure 3.18(b) for low positive V_{GS} values, however the most obvious feature of the graph is the increase in I_G (in the negative direction) for increasingly negative values of V_{GS} . Whilst this characteristic may be expected if there is an electrical connection - and hence a decrease in resistance - between gate and source through the dielectric (by Ohm's law), it is not observed for the device made with no P3HT layer. It is unclear at this stage as to exactly why this difference exists, however both Figure 3.20(a) and (b) show much higher I_G values than for the standard device (Figure 3.5) and this increase in $|I_G|$ is responsible for the changes in output characteristics.

It is possible to apply a simple equivalent circuit model to help visualise the behaviour of devices when the PEDOT:PSS of the gate is allowed to make contact with the source and drain electrodes through the PVP layer (either by an offset gate layer or by removal of the P3HT layer). Figure 3.21 shows a simple equivalent circuit for a OTFT adopted from a widely used model applied to poly-silicon TFTs [92, 93]. In the diagram, Z_D is the contact impedance of the drain electrode, Z_S is the contact impedance of the source, Z_{GD} is the impedance between gate and drain, Z_{GS} is the

impedance between gate and source, and I_{OTFT} is the current flowing in the P3HT due to any given bias voltages. For the highest performance, Z_D and Z_S should be as low as possible, whilst Z_{GD} and Z_{GS} should be as high as possible to minimise current flowing into the gate (I_G). In the case where the PEDOT:PSS is mis-aligned, Z_{GD} and Z_{GS} are lower (for the reasons outlined above), and therefore inducing higher I_G levels and allowing current to flow around the P3HT layer meaning relatively less contribution to I_D from I_{OTFT} . This model fits the behaviour observed in Figure 3.19 where the two output characteristics resemble that of a standard OTFT (where I_{OTFT} is the dominant contributor to the characteristic) superimposed with the response seen in Figure 3.18 in which there is no P3HT layer and hence I_{OTFT} is zero.

As well as highlighting the susceptibility of device performance to small changes in one aspect of the fabrication procedure, this experiment also confirms the tendency of a PVP film to allow PEDOT:PSS to diffuse through it as indicated by the PVP thickness study (Section 3.2.2).

3.2.7 V_{DS} Scan Rate Investigation

By studying the changes in the characteristics of devices when V_{DS} is scanned at different speeds, it was hoped that further insight could be gained into their operation. Whereas OFETs can now reach switching speeds approaching their conventional silicon-based counterparts (well in excess of 1 MHz) [94, 95], electrochemical transistors tend to be limited to the 1 to 10 Hz range [96, 97]. If the mechanisms involved in current modulation have an electrochemical component rather than being purely electrostatic or electric-field dependant, the rate of change of V_{DS} when measuring the output characteristic would be expected to have an impact on the measurement.

Rather than keeping the V_{DS} step size constant and changing the time between steps (as may seem intuitive), the V_{DS} step size itself was altered and the time interval between steps kept constant. This way of modulating V_{DS} scan rate was necessary due to limitations of the software controlling the Keithley meters. V_{DS} step sizes of 0.05 V, 0.1 V (the standard step size), 0.2 V and 1 V were used in this study. The time between V_{DS} steps in each case was 1 s, and V_{GS} was scanned from $V_{GS} = 1\text{ V}$ to $V_{GS} = -2\text{ V}$. The transfer characteristics was taken at $V_{DS} = -1\text{ V}$ instead of the normal $V_{DS} = -1.5\text{ V}$ since in the case where 1.0 V or 0.2 V steps are used, there is no reading at $V_{DS} = -1.5\text{ V}$.

As Figure 3.22 shows, the transfer characteristics are very similar for the three slowest scan speeds, but there is relatively little current modulation in the case where V_{DS} is scanned at 1 V/s. This observation provides further indication that the mechanisms for current modulation in the devices are likely to be primarily ionic and/or electrochemical in nature since such a process would likely be slow compared with the

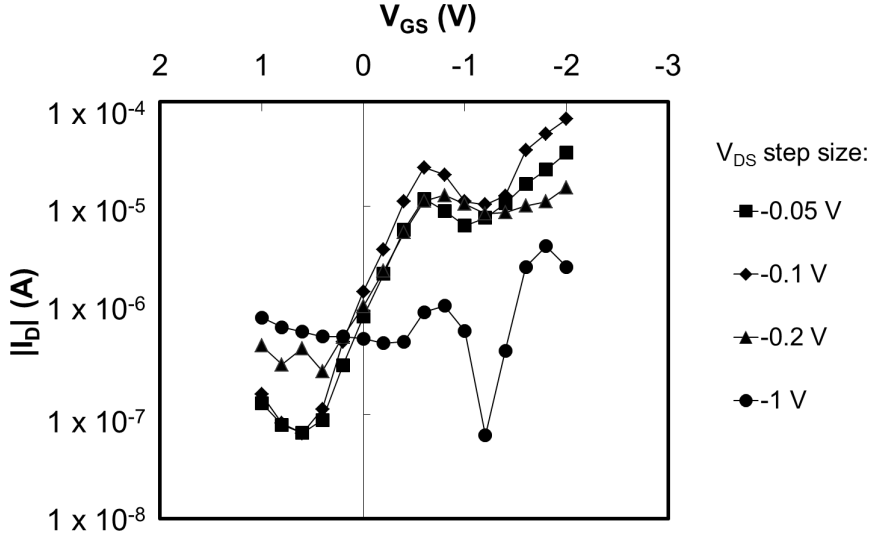


FIGURE 3.22: Transfer characteristics (obtained from output characteristics) of standard OTFTs measured at different V_{DS} scan rates.

formation of a layer of charge along the semiconductor/dielectric interface (the alternative mechanism suggested by Sandberg et al. [27]).

The decrease in current observed in all the transfer curves at $V_{GS} \approx -1.4$ V is consistent with previous measurements 3.3. However, the reason why a drop in I_D is observed at this point followed by a subsequent increase for more negative values of V_{GS} is unclear and could be a topic for future investigation.

The experiment of sweeping V_{DS} at different speeds has shown that the flow of current between source and drain is affected by mechanism(s) which depend on V_{DS} (rather than only V_{GS}) and occur on a relatively slow time scale. This observation further supports the notion of electrochemical doping occurring in the device as a current modulation mechanism.

3.2.8 Two-terminal Measurements

Several different combinations of the materials used in the standard OTFT have been cast on the normal ITO-on-glass substrates and their “two terminal” electrical characteristics measured. The reason for carrying out these experiments is to determine the conductivity of the individual components of the transistors and thus better understand the operation of the device as a whole.

Measurements were simply conducted by measuring current as a function of the voltage applied across the material connecting the two ITO pads normally used as the source and drain electrodes in the OTFTs. In these measurements there is no gate

connection, and a voltage range of -2 V to 2 V is used. Current-voltage (I-V) measurements were conducted on four different combinations of materials: P3HT, PVP, P3HT/PVP and P3HT/PVP/PEDOT:PSS, although the currents through the PVP only film were too low to be reliably measured with the available equipment and are not shown here.

For the P3HT only film, a linear I-V relationship is observed (Figure 3.23(a)). An increase in P3HT conductivity when PVP is deposited on top of it is observed (Figure 3.23(b)). This is despite the fact that the PVP film itself has very low conductivity compared with P3HT (too small to measure, as mentioned above), so the change in conductivity must be due to some interaction between the P3HT and the PVP rather than the result of simply having two resistors in parallel. Bäcklund et al. also observed an increase in the conductivity of P3HT when a PVP film is applied [57]. They suggest that this observation is due to the phenol groups in the PVP forming a dipole near the P3HT interface and hence inducing a region of increased conductivity in the semiconductor, which could also explain the change in conductivity observed here.

When PEDOT:PSS is drop-cast on top of the PVP layer, a further, more significant increase in current is observed, however this time the I-V relationship is non-linear (Figure 3.23(c)). This increase in current is further evidence of PEDOT:PSS contributing significantly to the current between source and drain in these devices prior to any applied V_{GS} . There appears to be an ambipolar diode-like response with a forward voltage drop of about 0.5 V in each direction. Recall that the two-terminal structure is entirely symmetrical (aside from any unintentional lateral bias in the drop-cast PEDOT:PSS gate position), so this ambipolar characteristic is expected. The diode-like response is what can be expected from a metal-semiconductor (Schottky) interface [98], so the P3HT/PVP/PEDOT:PSS structure can be thought of as being two such interfaces in parallel.

These two-terminal measurements provide another insight into the workings of this type of OTFT. The PVP dielectric layer affects the conductivity of the P3HT, although does not allow electrical conduction itself, and the PEDOT:PSS gate material further increases the conductivity between the source and drain electrodes.

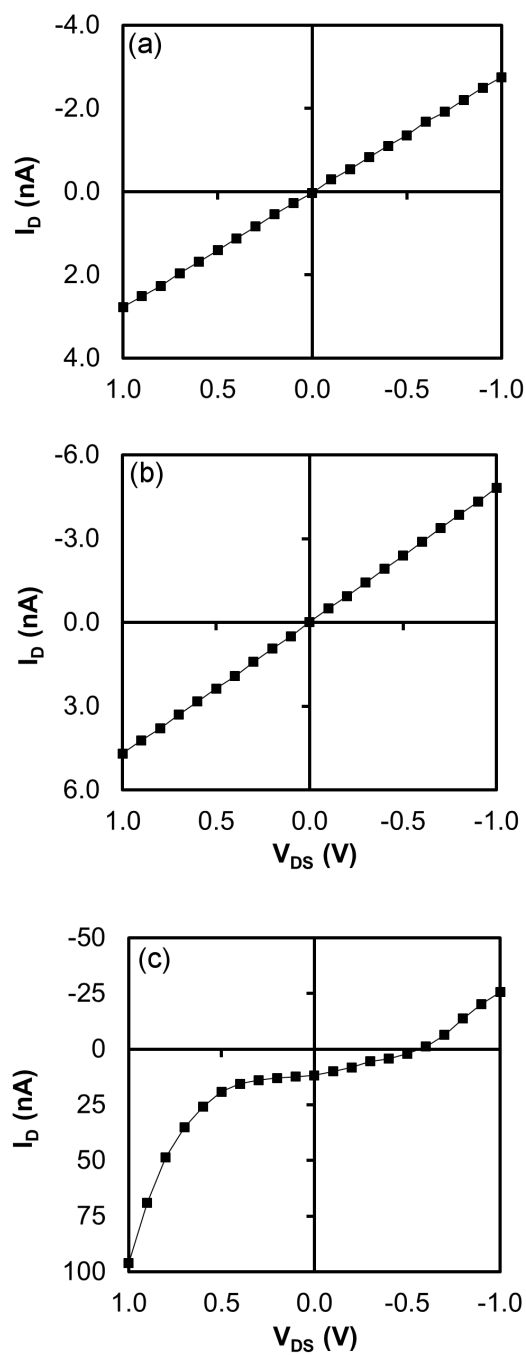


FIGURE 3.23: Two terminal I-V characteristics between the source and drain pads of a standard OTFT measured after each layer is deposited: (a) P3HT only, (b) P3HT/PVP, and (c) P3HT/PVP/PEDOT:PSS.

3.3 Mechanism Determinations and Estimations

Firstly, it is worthwhile discussing again the use of the generic term “organic thin-film transistor” as opposed to the widely used “organic field effect transistor” (OFET). As was mentioned in Chapter 1, the term OFET is used in literature to describe a wide variety of organic transistors [47, 48, 81]. However, unless the device in question employs a conventional dielectric across which an electric field is established to induce a region of higher (or lower) conductivity in the semiconductor layer, it is somewhat misleading to label the device an OFET. In this chapter, evidence has been presented which shows that the mechanisms causing transistor-like behaviour in the OTFTs presented here involve ionic movement within the dielectric layer and/or some electrochemical effects. The data supports the notion that devices of this type should not be labelled FETs.

Varying the thickness of the P3HT layer showed that transistors can be fabricated using a wide range of semiconductor thicknesses: devices with P3HT thicknesses of 25 nm through to 447 nm all showed characteristics expected for a standard device. I_{ON} showed an increase with increases in P3HT thickness. However, the changes in I_{ON} were not proportional to the changes in P3HT thickness. This relationship is indicative that the P3HT film is not bulk-doped and that the majority of doping is restricted to a region close to the dielectric interface.

From Section 3.2.2, it appears that the current levels (both I_{ON} and I_{OFF}) of the devices are certainly not enhanced by increased PVP thickness. On the contrary, there appears to be a decrease in I_D with PVP thickness. Considering I_{OFF} , PVP is seemingly acting as a physical and/or chemical barrier to the P3HT against dopants from the PEDOT:PSS, and therefore the contribution to I_D from dopants in the PEDOT:PSS can be controlled somewhat by varying the thickness of the PVP, although this change is not so drastic as to change the general behaviour of the device. For PVP thicknesses between 451 nm and 2324 nm, working transistors were fabricated. This result also goes some way to showing that there is no ionic contribution to current modulation from the PVP itself. This hypothesis is supported by the two-terminal PVP film characterisation in which there is no measurable current.

The experiment of comparing the characteristics of devices when measured in air and in a dry nitrogen environment indicated that a component in air is responsible for activating the current modulation mechanism. It is possible that this component is humidity since it is known that PVP is hygroscopic and hence will readily attract water. If the current modulation was purely due to an electric field, there should be no difference in the output of the devices when measured in these two environments. This result supports the findings of Österbacka’s group who performed similar experiments [27, 49].

Section 3.2.4 shows degradation of I_D levels once a threshold value of V_{GS} of between -0.4 V and -0.6 V has been exceeded. This data is indicative of an electrochemical change occurring in the devices. Indeed, it has been found previously that over-oxidation of polythiophenes reduces their electrical conductivity [99, 100]. The

fact that there is no degradation is observed when the voltage across the source and drain electrodes is taken to -2 V indicates that the species for this over-oxidation do not move between source and drain, only in the dielectric (i.e. between the gate and the other two electrodes).

Assuming that ionic movement within the dielectric is the major contributor to the device behaviour, there are two possibilities for these species' involvement in current modulation (ignoring any permanent electrochemical changes): bulk electrochemical doping of the P3HT or electrochemical and/or electrostatic doping of the P3HT near the dielectric interface [27]. Figure 3.24 shows diagrammatically each mechanism and their neutral (or cut-off) state ((a) and (d)), linear regime ((b) and (e)) and saturation regime ((c) and (f)). In both cases, the saturation regime occurs when the magnitude of the V_{DS} is greater than that V_{GS} and the region of increased conductivity changes shape. The increase in V_{DS} is compensated for by an equivalent increase in low conductivity semiconductor in the current path, keeping I_D relatively constant.

At $V_{GS} = 0$ V, as V_{DS} becomes more negative, the charge at the drain from both the source and gate's point of view becomes more negative, which causes a shift in the charge carriers towards the drain. This ionic movement, in turn, creates a region of fewer charge carriers and lower conductivity. This region becomes larger as V_{DS} becomes more negative, leading to the saturation.

At more negative values of V_{GS} , and at $V_{DS} = 0$ V, the gate is negative compared with both the source and drain and two layers of charge are formed whereby cations are drawn towards the PVP/PEDOT:PSS interface, and anions drift towards the P3HT/PVP interface. This process in turn increases the concentration of positive charge carriers in the P3HT layer near the PVP interface. As V_{DS} becomes more negative, the location of the region of charge carriers again changes, attracted by the relatively negative drain, leading to pinch-off and saturation.

For small positive values of V_{GS} , it is conceivable that positive charge carriers in the PVP layer are forced away from the gate electrode and towards the P3HT/PVP interface. This in turn disperses the charge carriers in the P3HT layer, resulting in lower I_D levels than for $V_{GS} = 0$ V.

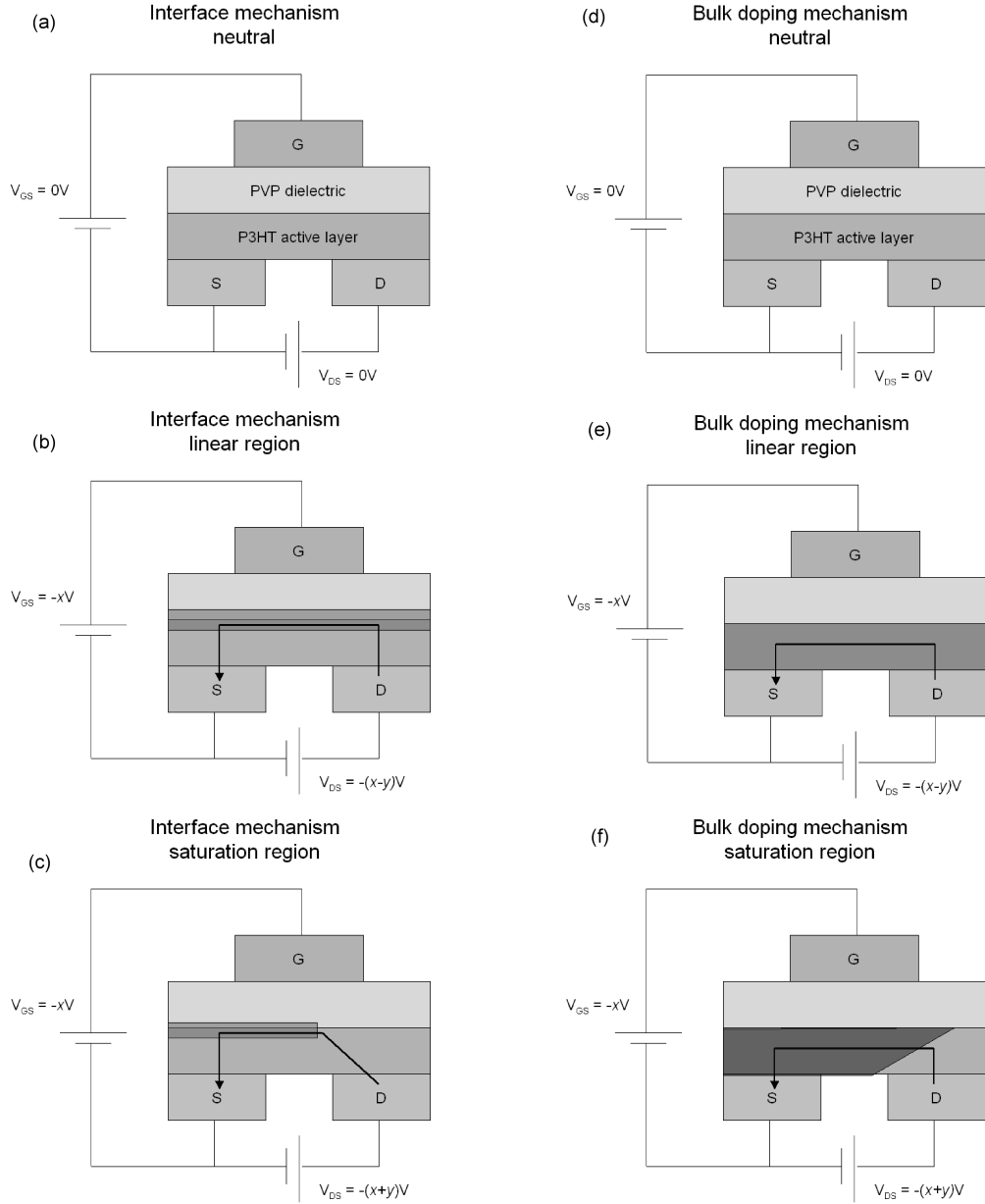


FIGURE 3.24: Diagram of interface and bulk-doping mechanisms in neutral state, linear region and saturation region: (a), interface mechanism (neutral); (b), interface mechanism (linear region); (c), interface mechanism (saturation region); (d), bulk-doping mechanism (neutral); (e), bulk-doping mechanism (linear region); (f) bulk-doping mechanism (saturation region).

3.4 Conclusion

The observations presented in this chapter indicate a strong dependence of the operation of the standard OTFTs on ionic movements in the PVP layer and electrochemical doping and de-doping of the P3HT layer. The ions involved in these processes are likely liberated from water attracted to the hygroscopic PVP layer as well as protons contributed by the PEDOT:PSS. Furthermore, protons from the PEDOT:PSS appear to increase the conductivity of the P3HT without any influence from V_{GS} . As was summarised in Section 3.3, it seems likely that doping in the interfacial area between the P3HT and PVP layers, rather than bulk-doping, is the most likely candidate. These findings agree with the conclusions reached by Sandberg, Bäcklund and Kaihovirta et al. in Österbacka's group [27, 48, 49, 57, 84, 85], however further understanding has been revealed of the characteristics of such devices and the films within them.

Although when compared with conventional FETs these devices do not compare favourably in terms of some parameters normally associated with transistor performance, their excellent performance in terms of operating voltage makes them ideal candidates for use in sensing applications. In order to improve the current modulation ratio of these OTFTs, it is desirable to increase I_{ON} , decrease I_{OFF} , or, ideally, both. Chapter 4 will focus on using a different dielectric material to limit the doping by PEDOT:PSS of the P3HT layer in an effort to decrease I_{OFF} , whilst still maintaining the low-voltage operation which is important to the potential applications of the device.

4

Poly-vinylpyridine as a Dielectric

In the previous chapter, OTFTs employing the hygroscopic dielectric PVP were presented, their performance assessed and the mechanisms involved in their operation investigated. Although these transistors had the advantage of operating at low voltages (achieving full current modulation at $|V_{GS}| < 1$ V) their I_{ON}/I_{OFF} ratio was quite low (in the order of 100). In Chapter 3 we showed that this low voltage operation was due to movement of ionic species (contributed both from the PEDOT:PSS gate solution and the surrounding atmosphere) within the PVP dielectric and the subsequent doping and de-doping of the P3HT layer, primarily at the P3HT/PVP interface. This mechanism is in contrast to conventional field-effect devices which rely on an electric field being established across the dielectric layer which modulates the conductivity of the semiconductor. It was suggested that their performance could be improved either by increasing I_{ON} levels or lowering their I_{OFF} levels. I_{OFF} is relatively high when compared with similar types of devices already reported and indeed for OTFTs in general [15, 49]. In this chapter, we present an alternative dielectric material to PVP with the aim of facilitating lower I_{OFF} levels and hence improving device performance.

4.1 Introduction to Poly-vinylpyridine

Evidence presented in the previous chapter suggested that the PEDOT:PSS suspension used for the gate electrode in the standard devices was responsible for doping the P3HT semiconductor. This doping led to an increase in “base” P3HT conductivity (without any influence by a voltage at the gate), which was the main reason for a high I_{OFF} value. Furthermore, it was shown that the PVP dielectric layer is not effective in protecting the P3HT film from being doped by the PEDOT:PSS gate material. Although

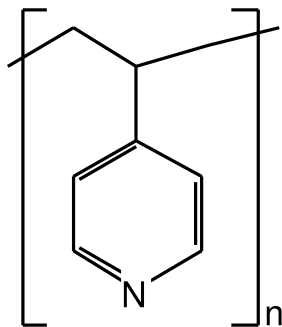


FIGURE 4.1: PVPy chemical structure.

I_{OFF} fell slightly with increased PVP thickness (Section 3.2.2), indicating that PVP provides a weak physical barrier between the PEDOT:PSS and the P3HT, I_{OFF} levels of the standard devices were significantly larger than the 2-terminal current through a bi-layer of P3HT/PVP over the same voltage range.

The PEDOT:PSS solution used in the fabrication process is acidic [76] and abundant in protons and PVP is also acidic in character, readily donating H^+ ions. It seems reasonable to hypothesise, therefore, that if a chemically basic hygroscopic material could be used as the dielectric, it could be more effective in protecting the P3HT from this intrinsic doping by reacting with and binding the protons in the PEDOT:PSS solution, thus inhibiting their ability to dope the P3HT.

Poly-vinylpyridine (PVPy) is a hygroscopic material with the desired basic nature which was employed instead of PVP as the dielectric of the OTFTs presented in this chapter. PVPy has already been the subject of some research into its properties as an organic dielectric [101]. It has also been the subject of a wide variety of studies where it has been used with other materials to form composite dielectric films [102, 103]. However, its use as a dielectric in transistor applications has been limited to hybrid organic-inorganic devices [104]. The chemical structure of PVPy can be seen in Figure 4.1. The basic nature of PVPy is due to the lone pair of electrons near the nitrogen atom of the pyridine ring.

Exactly how the basic nature of PVPy would manifest into changes in device performance was unclear prior to characterisation. Ideally, PVPy's hygroscopic nature would allow the same low-voltage transistor behaviour as in the PVP-based devices whilst restricting the inherent bulk P3HT doping caused by PEDOT:PSS deposition. However, there was also the possibility that the ions would be inhibited too much to allow the flow of ions throughout the device and thus restrict current modulation. The way that PVP and PVPy donate and bind H^+ ions respectively is shown in Figure 4.2.

PVPy dielectric films were prepared and deposited in the same way as the PVP

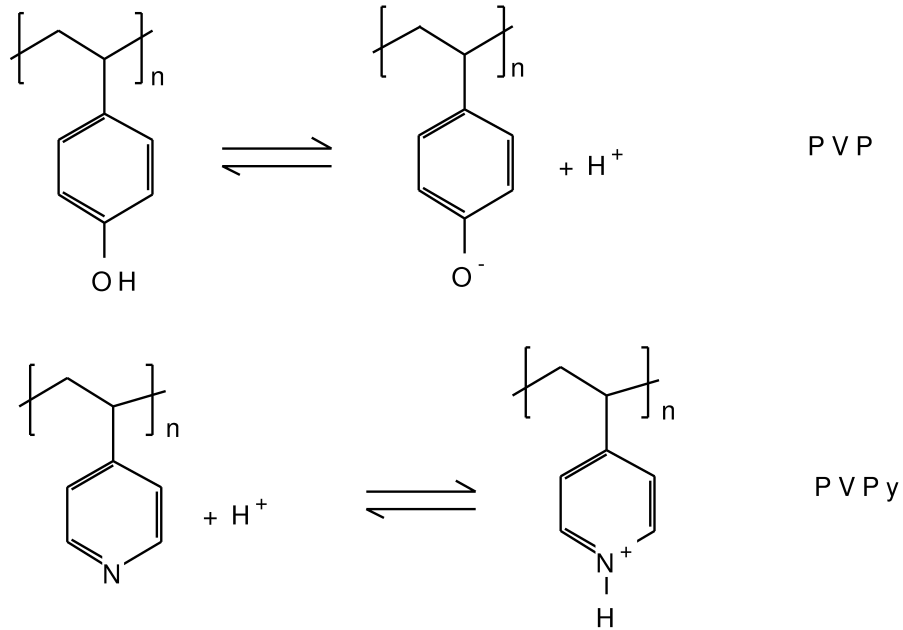


FIGURE 4.2: Interactions of PVP and PVPy with protons. Protons tend to bind to the pyridal groups on the PVPy, whereas PVP tends to donate protons.

dielectric films (as described in Chapter 2) at the same concentration by weight in the same solvent (80 mg/mL in ethanol). The thickness of the films was measured to be 555 ± 38 nm by profilometry, which is slightly thicker than PVP films (483 to 493 nm) spun from the same concentration.

4.2 Device Performance and Characterisation

Figure 4.3 shows the typical output characteristic of device employing a PVPy dielectric instead of the PVP layer used previously. As with the PVP-based OTFT, there are clearly defined linear and saturation regions as well as modulation of I_D with V_{GS} , indicating that a transistor with a PVPy dielectric has indeed been successfully fabricated. One significant change in the electrical characteristics compared with the PVP-based device is that both the I_{ON} and I_{OFF} levels have been greatly reduced, as highlighted by the transfer curve (extracted from the output characteristic measurement) shown in Figure 4.4. As such, the PVPy dielectric has been successful in reducing the I_{OFF} of the device as hypothesised - the typical I_{OFF} of these devices (at $V_{GS} = 0$ V) is about 1×10^{-8} A, which is over one order of magnitude lower than the average I_{OFF} of the PVP-based devices (approximately 7×10^{-7} A). However, I_{ON} is also significantly lower when compared with the PVP device, such that the current modulation ratio is of the same order (between 10 and 100).

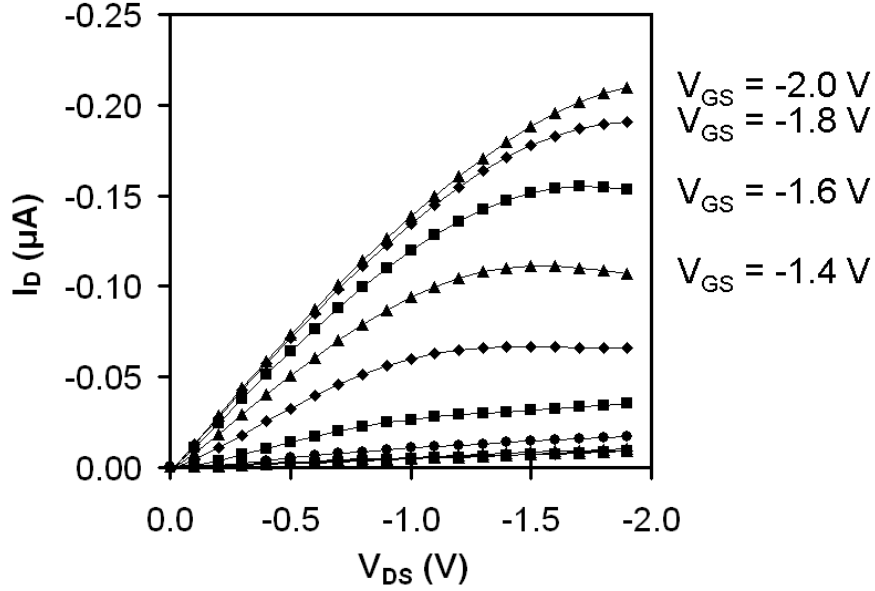


FIGURE 4.3: P3HT/PVPy/PEDOT:PSS device output characteristic.

The two terminal I-V data for P3HT/PVP/PEDOT:PSS “tri-layer” constructs shown in Figure 4.5 is consistent with the PVPy preventing the doping of P3HT by protons from the PEDOT:PSS thus leading to a lower I_{ON} and I_{OFF} in the devices (these measurements are made using the same method as the measurements taken in Section 3.2.8). Although the devices show some increased conductivity at higher values of $|V_{DS}|$, the current levels for $-1 \text{ V} \leq V_{DS} \leq 1 \text{ V}$ are only slightly higher than those observed in the two terminal case for pure P3HT films in the previous chapter. The increase in conductivity and non-linearity in current response for $|V_{DS}|$ higher than 1 V is similar to that shown previously for the P3HT/PVP/PEDOT:PSS two terminal measurements. This behaviour is consistent with the onset of a mechanism involving protons from the PEDOT:PSS solution (since such non-linearity is not observed for two terminal measurements on P3HT or P3HT/PVP).

Figure 4.6 shows the I_{OFF} levels for a typical PVP-based device and a typical PVPy-based device at $V_{GS} = 0 \text{ V}$ which confirms that the base conductivity of P3HT is much lower with a PVPy dielectric layer.

Although the introduction of PVPy has successfully reduced I_{OFF} , there is an increase in the required operation voltage; that is, they require a larger value of V_{GS} (by about 0.5 V) to initiate modulation of I_D . Although this change in V_{TH} would require

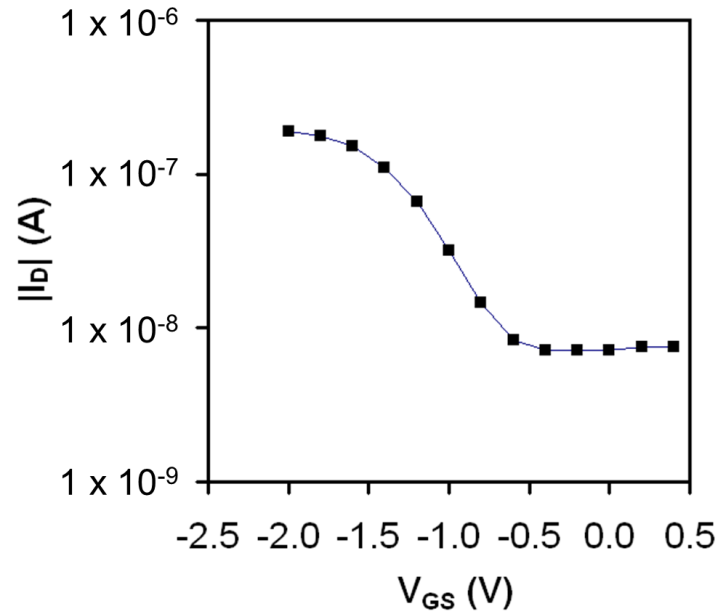


FIGURE 4.4: Transfer characteristic of a P3HT/PVPy/PEDOT:PSS device extracted from the output characteristic at $V_{DS} = -1.5$ V

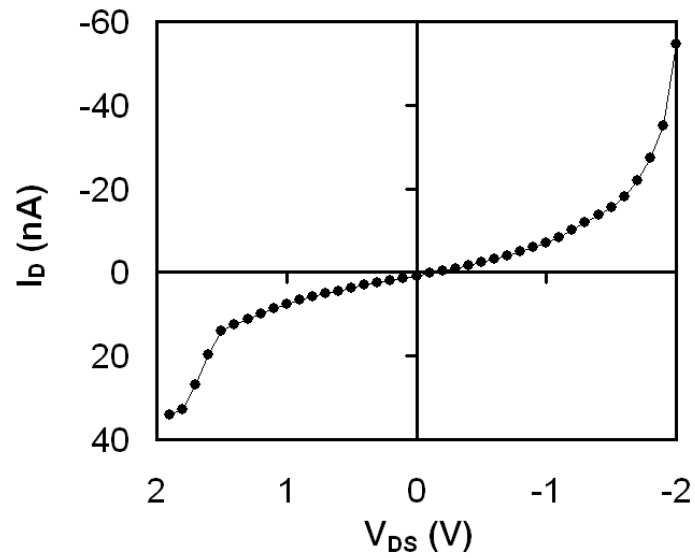


FIGURE 4.5: Two terminal conductivity of a P3HT/PVPy/PEDOT:PSS tri-layer.

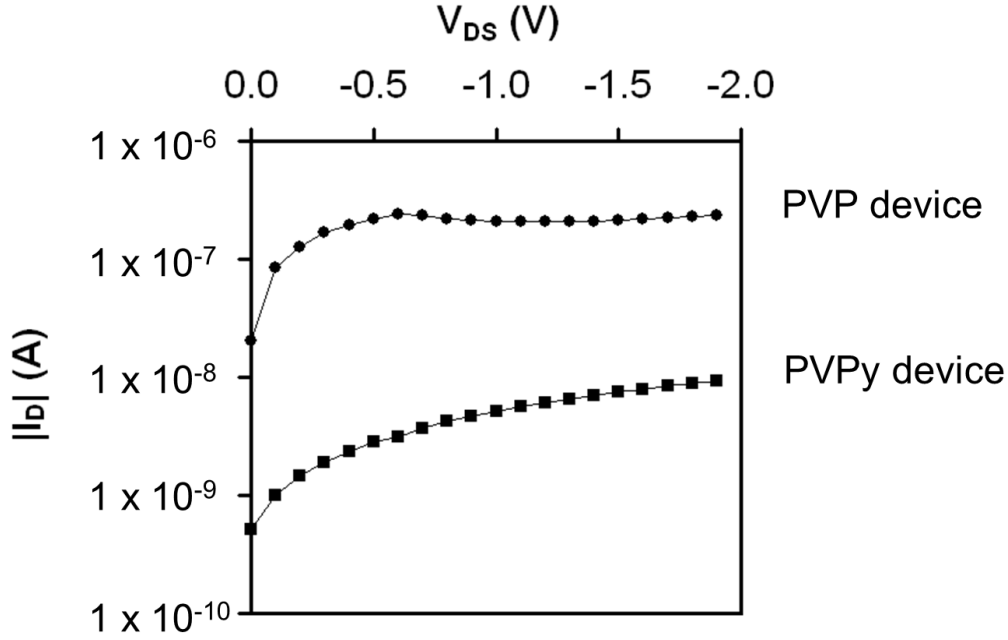


FIGURE 4.6: I_{OFF} levels for PVP and PVPy-based OTFTs.

a slightly higher operating voltage, it is not enough of a change to limit the practicality of the device and it can still be considered “low voltage operation”. From Figure 4.4 it can be seen that at $V_{DS} = -1.5$ V, there is almost no change in I_D until V_{GS} is more negative than -0.8 V, and I_{ON} is not reached until $V_{GS} \approx -2$ V. This behaviour is in contrast to the PVP-based devices which typically achieve full current modulation at $V_{GS} \approx -0.6$ V. The mechanism causing this increase in V_{TH} is likely the same as that which allows for the maintenance of a low conductivity value for P3HT (low I_{OFF}). That is, protons are much less mobile in PVPy compared with PVP.

Figure 4.7 shows the transfer characteristic of an OTFT with a PVPy dielectric at $V_{DS} = -1.5$ V measured by sweeping across a range of V_{GS} values in both directions three times for a fixed V_{DS} of -1.5 V at a scan rate of 50 mV/s. Even though there is some hysteresis in the different scan directions, the I_D values obtained are highly reproducible and there is no degradation or change in the current levels in subsequent scans. This result implies the lack of a permanent electrochemical effect in these PVPy-based devices at these voltage levels.

Figure 4.8 shows the gate leakage current values for the PVPy-based device. The I_G values of the PVPy-based devices are very low and are over an order of magnitude lower than their corresponding I_D values (for the same bias voltages). This result indicates a high gate (input) resistance which is desirable for many applications. The I_G

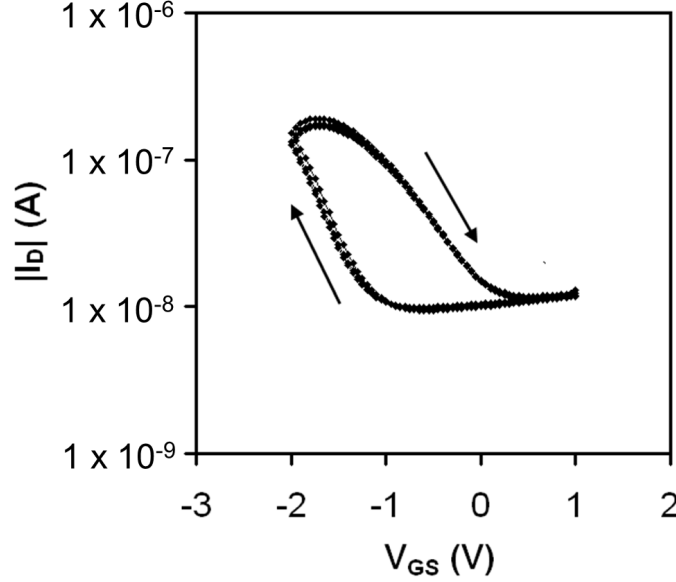


FIGURE 4.7: Transfer characteristic of P3HT/PVPy/PEDOT:PSS device measured directly at $V_{DS} = -1.5$ V. Scan speed = 50 mV/s.

values are also much lower than those of the PVP-based devices as shown in Figure 4.9, which is yet further evidence of the fact that PVPy prevents PEDOT:PSS from doping the P3HT's base conductivity level.

4.2.1 PVPy-based Devices in Dry Atmosphere

In order to determine the dependence of device behaviour on the humidity of the surrounding environment, OTFTs with a PVPy dielectric layer were characterised in a dry, nitrogen-rich glove box in the same fashion that the PVP-based “standard” devices were measured in Chapter 3. As was seen in Chapter 3, when devices with a PVP dielectric layer were left to equilibrate in a dry nitrogen environment and subsequently characterised, they showed no current modulation for the low operating voltages normally used to characterise the devices in air.

Figure 4.10 shows the output characteristic of an OTFT with a PVPy dielectric when measured in the glove box. As with the PVP-based device, there is no current modulation observed for the usual range of V_{DS} and V_{GS} . This observation indicates that the current modulation mechanism in PVPy devices also depends on humidity,

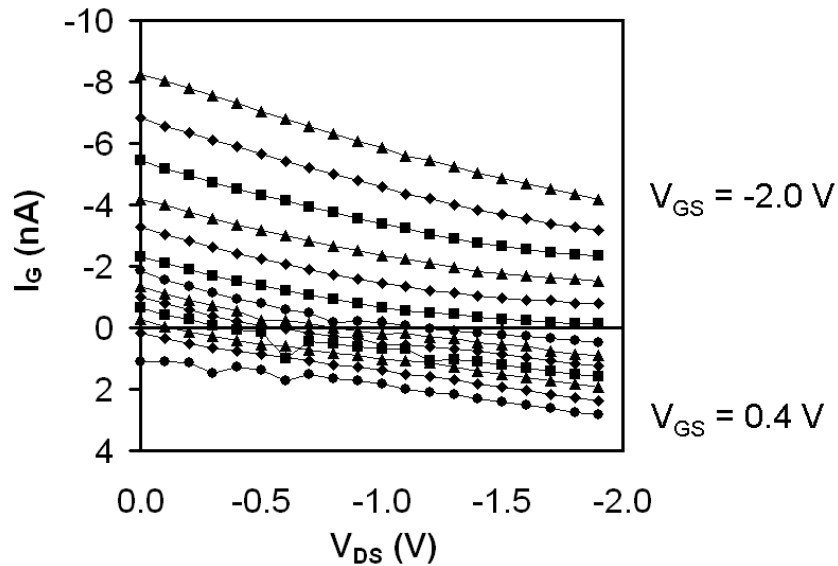


FIGURE 4.8: P3HT/PVPy/PEDOT:PSS device leakage currents from $V_{GS} = 0.4$ V to $V_{GS} = -2.0$ V.

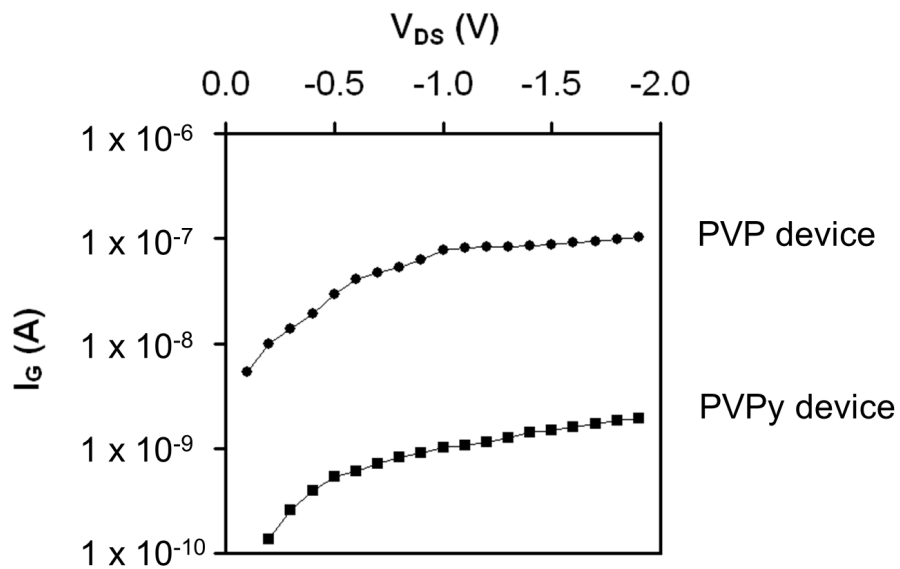


FIGURE 4.9: Comparison of I_G at $V_{GS} = 0$ V for typical PVP-based and PVPy-based devices.

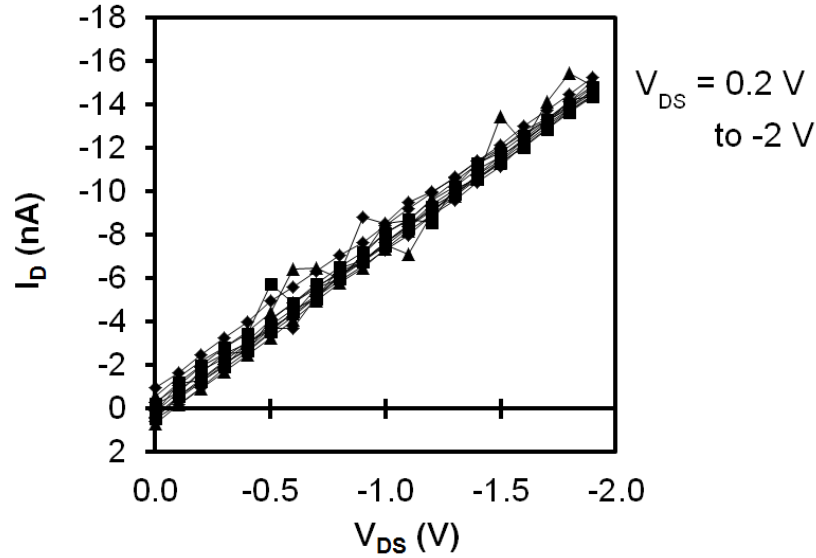


FIGURE 4.10: Output characteristic of an OTFT with a PVPy dielectric layer measured in a dry nitrogen environment.

and therefore on H^+ (and possibly OH^-) ion movement.

However, in this case, the I_D levels measured in the glove box are of the same order as the I_{OFF} values for the transistor (when measured under standard conditions). This result is in contrast to the behaviour of the PVP-based devices in which the I_D levels measured in the glove box were of the same order as their I_{ON} level. The low levels of I_D in the PVPy case demonstrates that the PVPy does not allow the PEDOT:PSS of the gate to dope the P3HT upon deposition, and that current is modulated through doping the P3HT to increase its conductivity rather than the suspected de-doping mechanism of the PVP-based devices.

4.2.2 PVPy-based Devices With an Offset PEDOT:PSS Gate

As was the case for the PVP devices, an experiment was conducted in which the PEDOT:PSS gate layer of a PVPy-based device was intentionally offset from the centre of the device such that it was deposited partially outside the P3HT semiconductor layer. Recall from Chapter 3 that in the case of the PVP-based devices, the offset gate resulted in a drastic change to the output characteristics.

Figure 4.11 shows the output characteristic (4.11(a)) and leakage currents (4.11(b)) for a device with a PVPy dielectric and a PEDOT:PSS gate which is offset on one side of the P3HT layer. In this case, it can be observed that the output characteristic has

not changed significantly from the “normal” PVPy device (Figure 4.3), although I_G levels have increased slightly upon offsetting the gate.

This data is further evidence of the strong interaction between PEDOT:PSS and PVPy. The PEDOT:PSS has been prevented from shorting the source or drain electrodes to the gate and hence “normal” device operation is maintained.

4.3 Discussion and Potential Improvements

As has been shown in this chapter, PVPy has been successfully introduced as a solution-processable polymer dielectric material for OTFTs. Data presented in Section 4.2 showed that utilising a PVPy layer (as opposed to a PVP layer) as the dielectric prevented the degrading effects on performance which occur by PEDOT:PSS diffusing through the device and making contact with the source and drain electrodes as well as doping the P3HT layer. This improvement is demonstrated clearly in Figure 4.6, which shows the difference in I_{OFF} , Figure 4.9, which shows the difference in I_G and Figure 4.11, which shows that normal transistor operation is retained even with an offset PEDOT:PSS gate. The way in which PVPy restricts the movement of protons within it compared with PVP is illustrated in Figure 4.12. In the PVP case, protons are free to move within the layer, however in the PVPy case, the pyridal groups bind some of the protons, restricting their movement.

The PVPy-based devices exhibit the same reliance on humidity as those with a PVP dielectric as exhibited in Section 4.2.1. This result shows that although the two types of devices behave differently, PVPy’s hygroscopicity is still important to device operation.

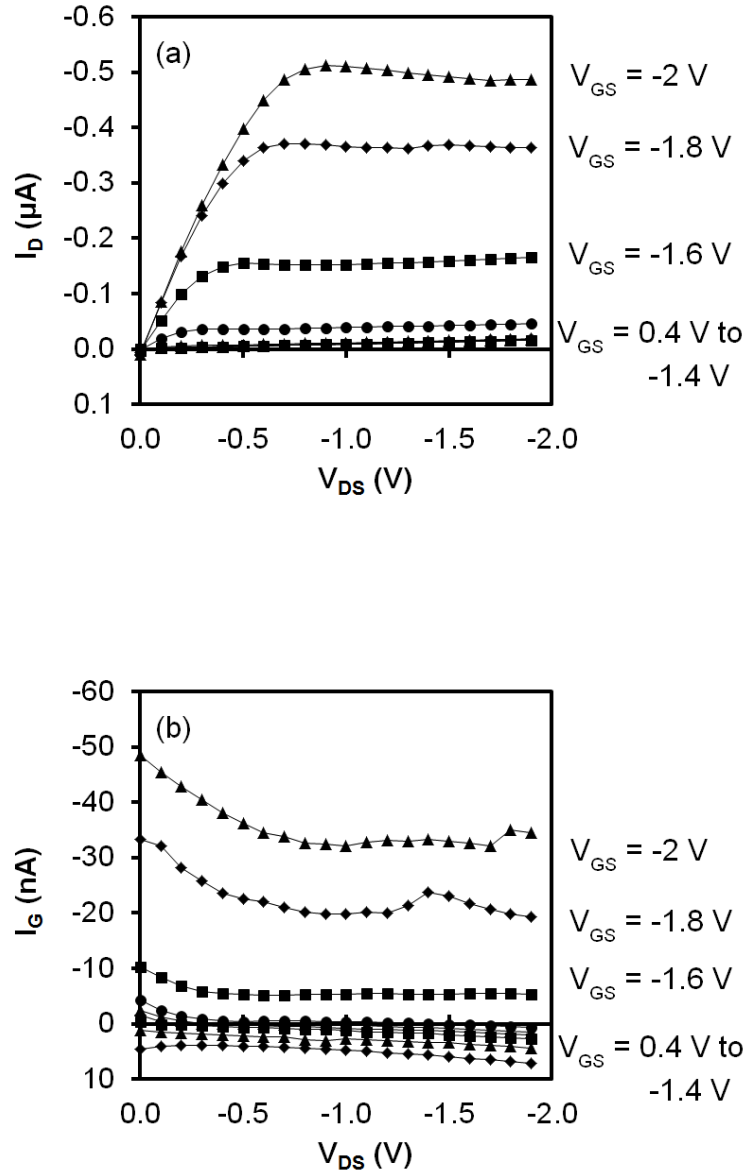


FIGURE 4.11: Output characteristic (a) and leakage currents (b) of an OTFT with a PVPy dielectric and a PEDOT:PSS gate offset to one side of the device.

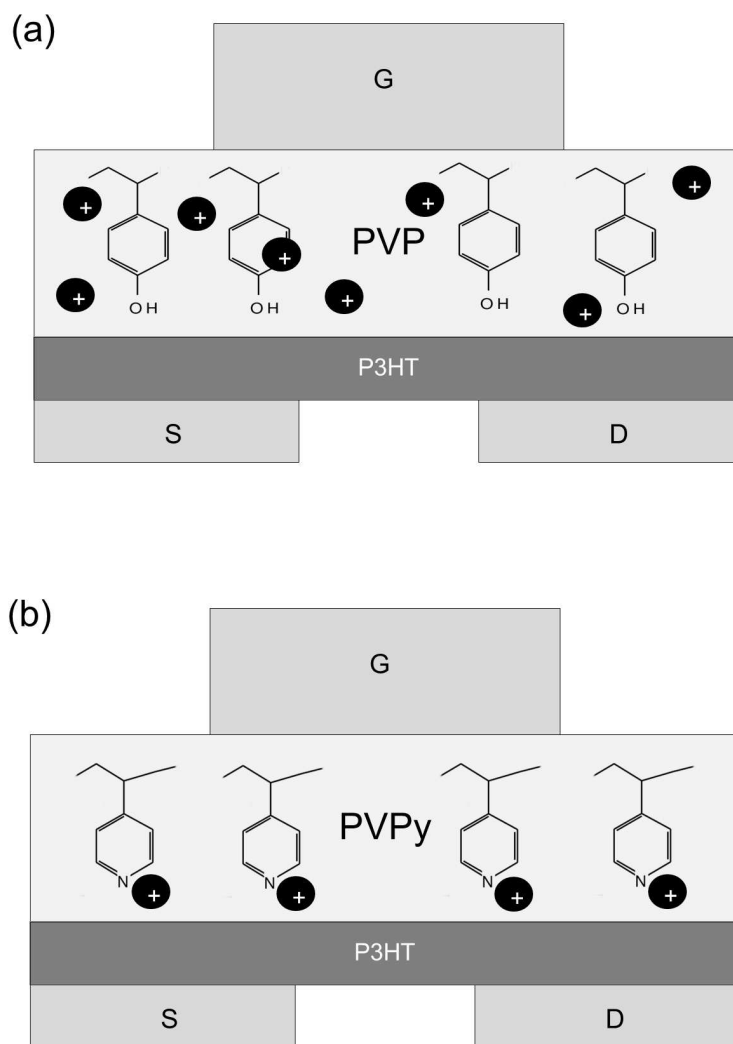


FIGURE 4.12: A conceptual image of how protons interact with (a) PVP, and (b) PVPy dielectric layers in a OTFT.

Although the use of PVPy instead of PVP solved the problem of high I_{OFF} values, it came at the cost of higher operating voltages and lower I_{ON} values. As a net result of the shift in both I_{ON} and I_{OFF} , the current modulation ratio remained of the same order of magnitude as the standard PVP-based devices. One way of improving the performance of OTFTs with a PVPy dielectric layer, therefore, would be to add ions into the dielectric layer in excess of those which occur simply due to the hygroscopic nature of PVPy. It is conceivable that this ion doping would have the effect of increasing current modulation, the mechanisms of which are known to be ionic in nature. Such an investigation is conducted in Chapter 5.

4.4 Conclusion

The data presented in this chapter is the first to introduce and extensively characterise polymeric OTFTs using plain PVPy dielectric layers. The aim of using PVPy as a dielectric to reduce the level of I_{OFF} by inhibiting the doping of P3HT by the PEDOT:PSS gate upon deposition. This goal was realised and I_{OFF} was reduced by approximately two orders of magnitude when compared with the PVP-based OTFTs. Furthermore, I_G was reduced when compared with the PVP-based devices since the movement of charge carriers was restricted in the PVPy due to chemical interactions as described in Section 4.1. This reduction in leakage current makes the devices more useful in applications where input impedance needs to be as high as possible.

In summary, it is clear that PVPy can be successfully used as the dielectric layer in the fabrication of low-voltage OTFTs. The PVPy prevents the PEDOT:PSS from doping (and hence increasing the conductivity of) the P3HT layer by chemically binding a large proportion of the protons contributed by the PEDOT:PSS. In terms of transistor parameters, this translates to lower I_{OFF} values.

In the next chapter, an investigation into adding ions (other than those offered by the PEDOT:PSS or attracted by the hygroscopic dielectric) into PVPy dielectric films is presented. This study was conducted with the aim of both increasing I_{ON} (thereby improving the current modulation ratio) and potentially lowering the operation voltage.

5

Ion-enhanced Performance of Organic Thin Film Transistors with Poly-vinylpyridine Dielectrics

The previous two chapters have introduced two types of OTFTs based on two different polyvinyl polymers as the dielectric layers. Firstly, Chapter 3 presented devices which relied on the hygroscopic nature on PVP to achieve low-voltage current modulation. In Chapter 4, another hygroscopic material, PVPy, was introduced in place of PVP which successfully reduced inherent doping of P3HT by the PEDOT:PSS gate material observed in the PVP-based devices. Although both types of devices achieved the objective of exhibiting transistor behaviour at low bias voltage levels ($|V_{GS}| < 2$ V), they both showed relatively low current modulation ratios (in the order of 100).

Much evidence has been presented so far in this thesis and elsewhere [27, 48] that ionic movement within the dielectric due to a voltage applied to the gate, and the subsequent electrochemical doping of the P3HT semiconductor, is responsible for the electrical characteristics of OTFTs with hygroscopic dielectrics. Therefore, it seems plausible that by introducing extra ions into the device (other than those which are liberated from the breakdown of water molecules ordinarily present in the transistor due to the hygroscopic dielectric), enhanced current modulation could be achieved. In this chapter, the results of a study are presented in which ions are added to the PVPy dielectric layer of OTFTs by mixing in an ionic salt at various concentrations into the dielectric solution. The resulting devices' characteristics are measured and the mechanisms involved in the devices are investigated.

5.1 Introduction to Lithium Perchlorate

Lithium perchlorate (LiClO_4) was chosen as an appropriate salt to use as the first dopant in this study due to its high solubility in ethanol (the solvent used for PVPy) and also because Li^+ is a physically small ion and hence was expected to be highly mobile within the PVPy dielectric, and its behaviour was expected to be closest to H^+ out of any candidates for dopant cations. It was hypothesised that a larger ion would be too immobile compared with the H^+ ions (which are largely responsible for the electrical behaviour of devices with a PVP or PVPy dielectric) resulting in higher operation voltages. The perchlorate ion (ClO_4^-) is relatively large and heavy when compared with Li^+ , so it was expected that it would be less mobile. The Li^+ and ClO_4^- ions could therefore conceivably move in a similar fashion to how Österbacka's group suggested that H^+ and OH^- ions may behave in their devices [27] due to the relative size of the ions.

LiClO_4 has already been successfully used as an ionic dopant in OTFT devices. The group of Frisbie et al. has previously reported using LiClO_4 in a poly-ethylene oxide (PEO) layer to form a "polymer electrolyte" as the dielectric layer of an OTFT in a number of publications [80–82]. These studies report current modulation ratios up to the order of 10^6 at relatively low operating voltages ($|V_{GS}| < 3 \text{ V}$) in devices with a P3HT semiconductor and gold source, drain and gate electrodes [80]. Devices employing other semiconductors, both polymeric and small molecule, were also successfully fabricated using the LiClO_4 -doped PEO [81, 82]. One of the disadvantages of using PEO is the difficulty it presents with regards to processability. The films made from the group of Frisbie were drop-cast and quite thick: in the order of $3 \mu\text{m}$ [81]. On the other hand, the doped-PVPy films presented here were spin-cast.

The devices presented in this chapter are fabricated using the same method as outlined in the Experimental chapter, the only variation being the addition of the dopant salt to the dielectric solution. The salt was added to the PVPy-ethanol solution at various concentrations prior to spin-coating.

5.2 Characteristics of Lithium Perchlorate-doped OTFTs

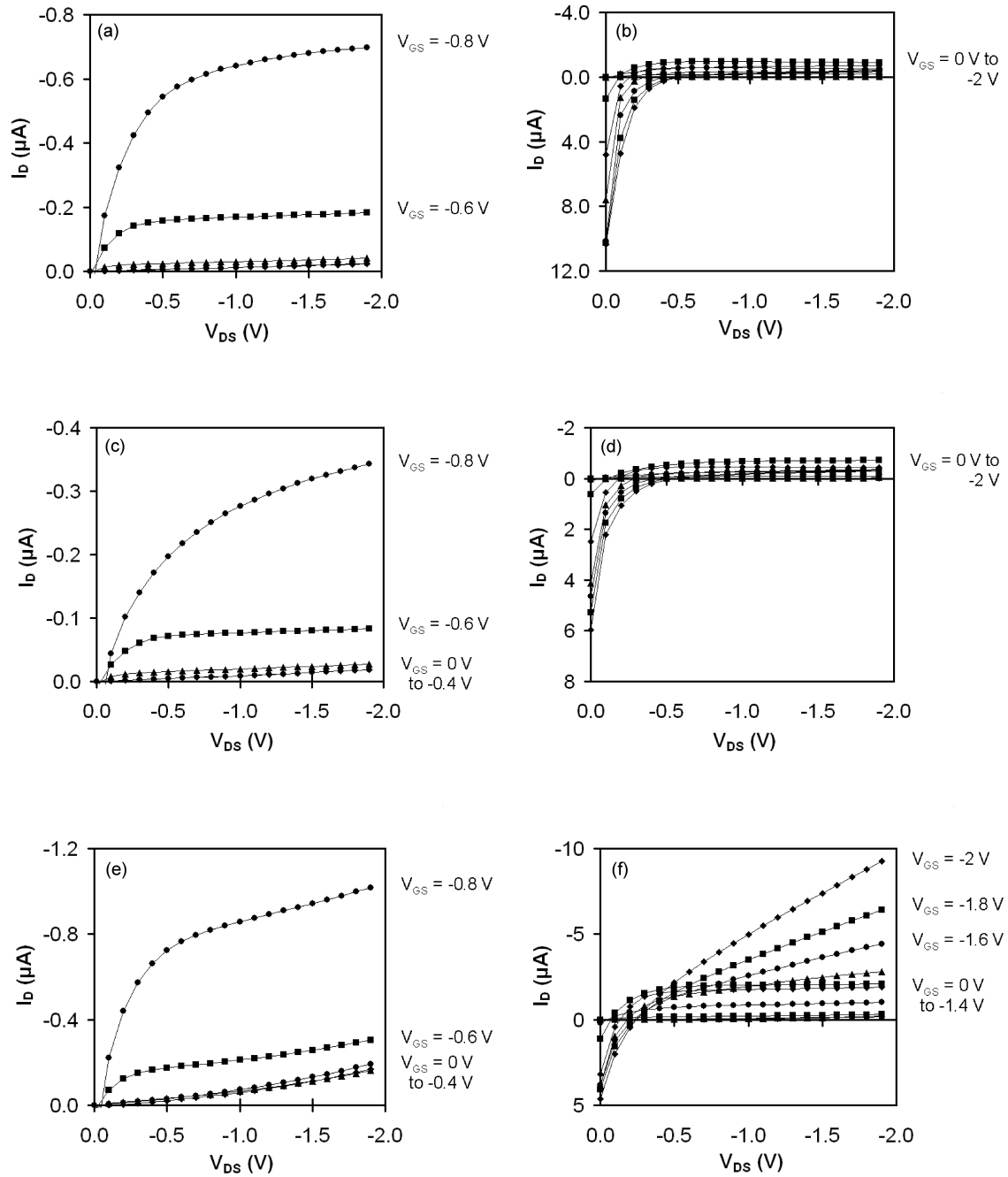
The first factor to determine when investigating this new type of OTFT is the optimal concentration of the added salt which gives the best device performance. Previous literature on electrolyte or ion-doped materials in OTFTs has not given an insight into the variation of device characteristics or performance for different concentrations of the dopant. In order to investigate the variation of electrical characteristics from different proportions of salt in a dielectric, devices were fabricated with six different concentrations of LiClO_4 in the PVPy-ethanol solution: 0.005 M, 0.01 M, 0.02 M, 0.05 M, 0.2 M and 0.5 M. Salt concentrations higher than this were not considered due

to the poor morphology of PVPy spun from solutions with 0.5 M LiClO_4 ; very rough layers were formed from this solution indicating that an upper concentration limit had been reached in terms of processability.

The output characteristics for devices with dielectrics spun from PVPy solutions doped with these six different concentrations of LiClO_4 are shown in Figure 5.1. For each device (and hence each LiClO_4 concentration), there are two different output characteristics shown for different ranges of V_{GS} : one is for $0 \text{ V} \geq V_{GS} \geq -0.8 \text{ V}$ and the other for $0 \text{ V} \geq V_{GS} \geq -2 \text{ V}$. Figures 5.1(a), (c), (e), (g), (i) and (k) show the output characteristics of these doped PVPy devices for $0 \text{ V} \geq V_{GS} \geq -0.8 \text{ V}$ in ascending order of LiClO_4 concentration. All of the devices exhibit similar electrical characteristics which resemble an undoped PVPy-based device (with the exception of the 0.5 M device, which will be discussed below). Since there is almost no difference in device performance and certainly no correlation in behaviour with salt concentration, it appears that any contribution to the output characteristic from the LiClO_4 is not observed for $0 \text{ V} \geq V_{GS} \geq -0.8 \text{ V}$.

Figures 5.1(b), (d), (f), (h), (j) and (l) show the output characteristics of devices in ascending concentration of LiClO_4 in PVPy over an extended V_{GS} range of $0 \text{ V} \geq V_{GS} \geq -2 \text{ V}$. In Figure 5.1(b) and Figure 5.1(d) (0.005 M and 0.01 M LiClO_4 respectively), V_{GS} values of -1 V and beyond induce almost no modulation of I_D and the leakage current dominates device performance (which can be seen by the relatively large positive I_D values at $V_{DS} = 0 \text{ V}$). However, for devices with LiClO_4 concentration greater than or equal to 0.02 M, a secondary current modulation mechanism is clearly observed, which we hypothesise to be contributed by the LiClO_4 . In Figure 5.1(f) (0.02 M LiClO_4), the onset of this mechanism can be observed as the values of I_D are increased slightly beyond that of the devices made with lower concentrations of LiClO_4 for V_{GS} up to -2 V. Figure 5.1(h) shows the output characteristic for 0.05 M LiClO_4 , and the I_D levels are further increased compared with the 0.02 M LiClO_4 device. Figure 5.1(j) (0.2 M LiClO_4) shows a much more significant increase in current modulation when compared with the 0.05 M LiClO_4 device over the same range of bias voltages. In this case, $I_{ON} \gg 1 \text{ mA}$ and we know from Figure 5.1(i) that $I_{OFF} < 0.1 \mu\text{A}$ so this is the first device which has been shown here having a current modulation ratio of well over four orders of magnitude. The 0.5 M LiClO_4 device's output characteristic (Figure 5.1(l)) exhibits lower I_{ON} values than the 0.2 M LiClO_4 device indicating that this 0.5 M is higher than the optimal salt concentration.

The transfer curves shown in Figure 5.2 show a comparison between these six devices and the magnitude by which I_D can be modulated in each case (at $V_{DS} = -1.5 \text{ V}$) is clearly observable. The 0.2 M LiClO_4 device has a current modulation ratio of over 10^5 at a very low operation voltage of $|V_{GS}| \leq 2 \text{ V}$. The I_{ON} levels increase with salt concentration aside from the 0.5 M device as already identified. However, the high I_{OFF} values for the 0.5 M device reduces its current modulation ratio. Looking at the



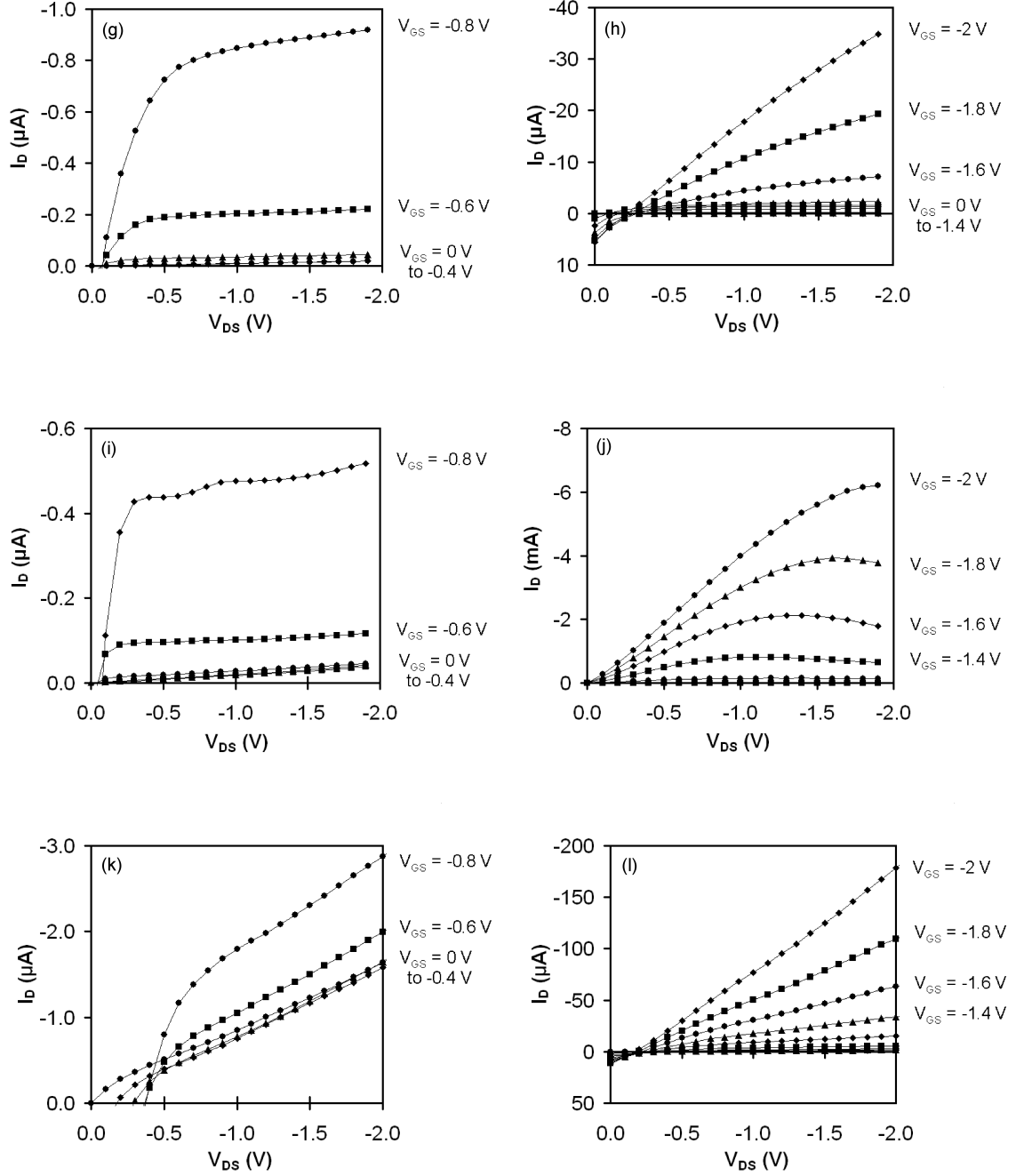


FIGURE 5.1: PVPy:LiClO₄-based OTFT output characteristics: 0.005 M LiClO₄, for (a) $0 V \geq V_{GS} \geq -0.8 V$ and (b) $0 V \geq V_{GS} \geq -2 V$; 0.01 M LiClO₄, for (c) $0 V \geq V_{GS} \geq -0.8 V$ and (d) $0 V \geq V_{GS} \geq -2 V$; 0.02 M LiClO₄, for (e) $0 V \geq V_{GS} \geq -0.8 V$ and (f) $0 V \geq V_{GS} \geq -2 V$; 0.05 M LiClO₄, for (g) $0 V \geq V_{GS} \geq -0.8 V$ and (h) $0 V \geq V_{GS} \geq -2 V$; 0.2 M LiClO₄, for (i) $0 V \geq V_{GS} \geq -0.8 V$ and (j) $0 V \geq V_{GS} \geq -2 V$; 0.5 M LiClO₄, for (k) $0 V \geq V_{GS} \geq -0.8 V$ and (l) $0 V \geq V_{GS} \geq -2 V$.

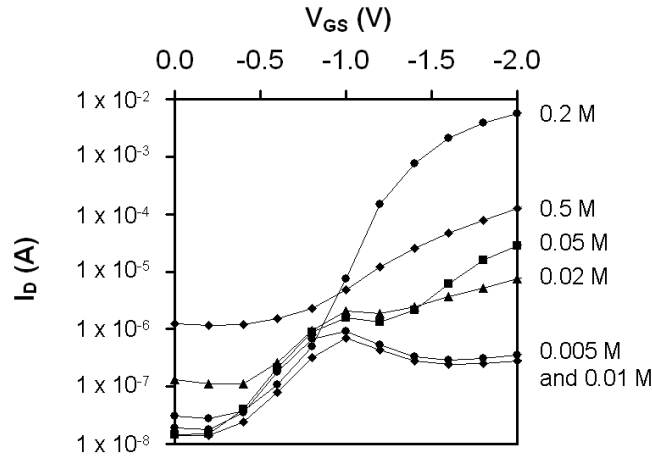


FIGURE 5.2: Transfer curves extracted from output characteristics of LiClO_4 -doped PVPy-based devices at different LiClO_4 concentrations.

devices with the lowest LiClO_4 concentrations, the 0.005 M and 0.01 M devices have transfer curves which are almost identical; this result confirms that there is no change in device behaviour until a certain concentration of salt is reached.

As noted above, the 0.5 M LiClO_4 device shows a different characteristic for the lower V_{GS} range ($0 \text{ V} \geq V_{GS} \geq -0.8 \text{ V}$) when compared with the devices of lower LiClO_4 concentration. This difference is in part due to the relatively high I_{OFF} levels. Recall that the reason the PVPy was introduced as a dielectric material in Chapter 4 was to prevent the PEDOT:PSS doping the P3HT layer and increasing I_{OFF} . It seems reasonable to speculate that the poor morphology of the dielectric when the salt concentration is 0.5 M (as noted above) results in the PVPy not performing its role of preventing PEDOT:PSS from doping the P3HT. Figure 5.3 shows the I_{OFF} levels at $V_{GS} = 0 \text{ V}$ for six devices whose output characteristics are shown above. This graph more clearly shows that the 0.5 M LiClO_4 device's I_{OFF} is significantly higher than the other devices.

Figure 5.4 shows the leakage current levels versus V_{GS} for the six different devices. This graph shows that even though the 0.5 M device has a high I_G level, the 0.2 M device (which has been shown to have the best output and transfer characteristics), also has a much higher leakage current than the other devices - in the same range as the 0.5 M device ($I_G > 10 \mu\text{A}$). Thus, once a given concentration of LiClO_4 is present in the PVPy layer, there are sufficient ions present to significantly increase its conductivity which in turn results in higher I_G values. Figure 5.5 shows $-I_G$ versus V_{DS} relationships for the different LiClO_4 concentrations at $V_{GS} = -2 \text{ V}$. The constant nature of the

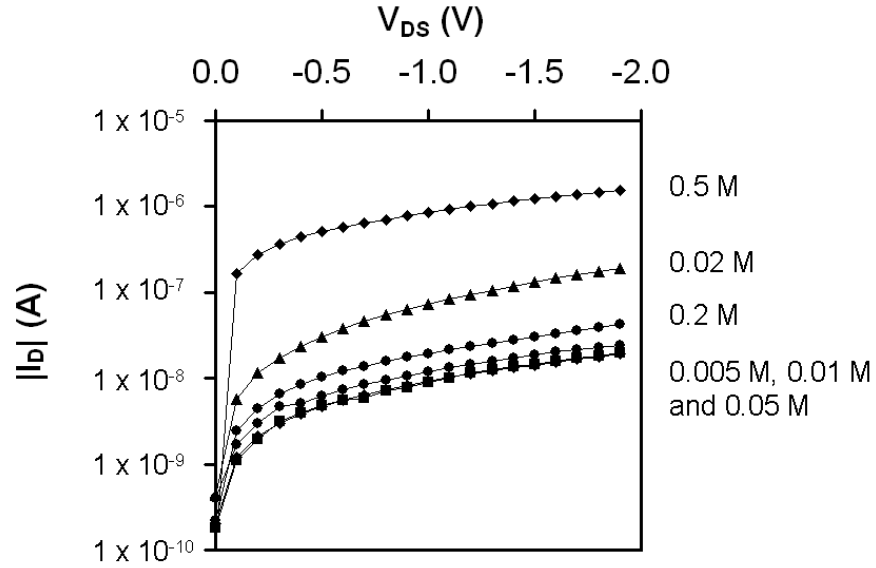


FIGURE 5.3: I_{OFF} at $V_{GS} = 0$ V for OTFTs with different concentrations of LiClO_4 in PVPy.

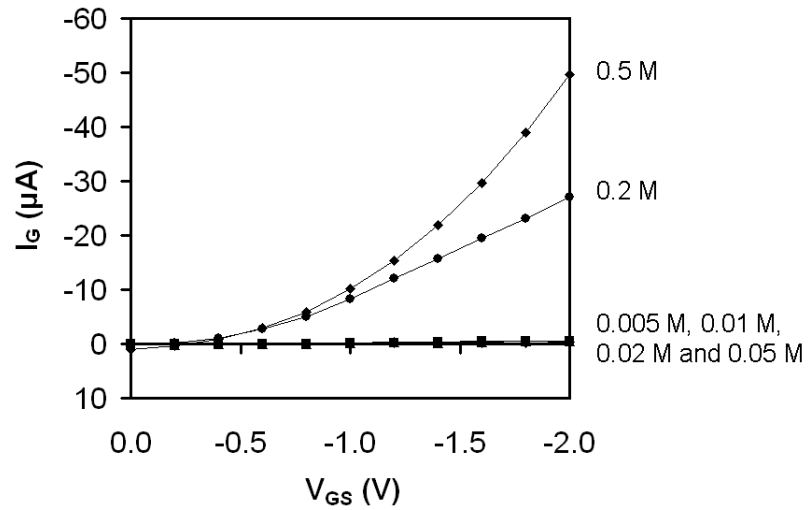


FIGURE 5.4: I_G values at $V_{DS} = -1.5$ V for OTFTs with different concentrations of LiClO_4 in PVPy.

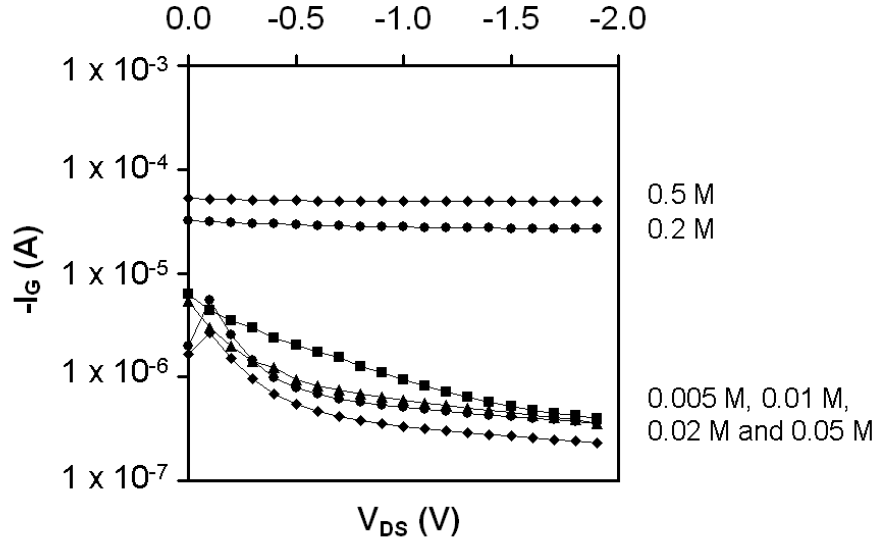


FIGURE 5.5: $-I_G$ values at $V_{GS} = -2$ V for OTFTs with different concentrations of LiClO_4 in PVPy.

relationship between I_{GS} and V_{GS} in the devices with the two highest concentrations is indicative of a saturation level of dopant being reached, for which (for a fixed V_{GS} value), changing the potential between source and drain does not induce a change in the conductivity between gate and source/drain because the entire dielectric layer has the same level of conductivity.

Since the devices made using 0.2 M LiClO_4 in PVPy give the best performance in terms of current modulation ratio, all subsequent experiments involving LiClO_4 -doped PVPy-based devices presented in this chapter were conducted at this concentration.

In order to gain further insight into the behaviour of these devices, measurements were taken of currents in the time domain. Figure 5.6 shows the absolute value of source current ($I_S = I_D + I_G$) versus time in the case where V_{DS} is fixed at -2 V and V_{GS} is switched from 0 V to -2 V after a few seconds as indicated on the graph. From the output characteristic of the equivalent device (Figure 5.1(j)), at these bias voltages an I_D of several milliamps and I_G in the order of tens of microamps (from Figure 5.4) would be expected to be induced (and hence $I_S \approx I_D$). Figure 5.6 shows that although it takes tens of seconds for I_S to reach its expected value, there is an initial fast increase in I_S (switching time < 10 ms), approximately of the order of the expected I_G . Therefore, it appears that upon switching V_{GS} , a change in I_G occurs rapidly that is the main contributor to I_S , but the mechanism which causes the larger increase in the magnitude of I_D needs some time to take effect. This slow effect could be electrochemical in nature and is likely preceded by ion layers forming at the dielectric interfaces on the same time scale as the switch in I_G .

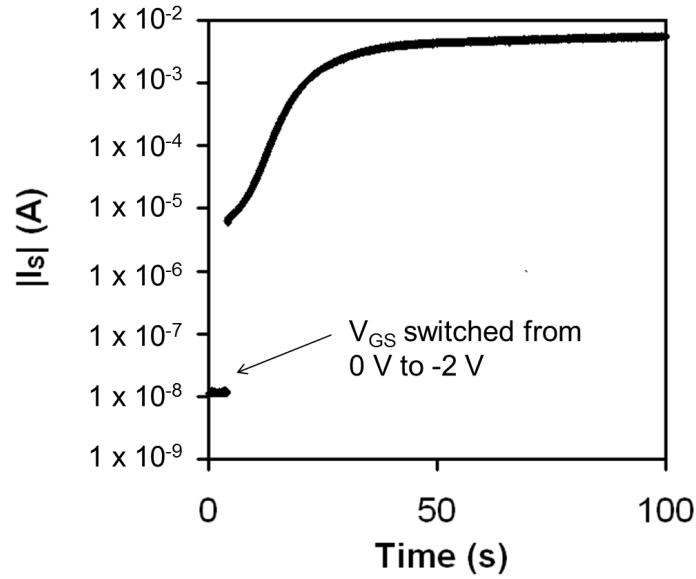


FIGURE 5.6: I_D versus time graph for an OTFT with a PVPy-LiClO₄(0.2 M) dielectric layer; sampling frequency = 100 Hz.

In a similar experiment, an AC signal was used at the gate of a device (as opposed to a single switch in V_{GS}) and I_S and I_G measured with time. A 10 Hz square wave switching between -2 V and 0 V was used for V_{GS} and V_{DS} was held at -2 V. Over a short time scale (Figure 5.7, inset), I_G follows I_S closely, and the switching speed of both is fast, occurring within one sampling period (1 ms). However, as the experiment continues the slow process which increases conduction between source and drain begins to contribute to and eventually dominate the shape of I_S versus time (Figure 5.7).

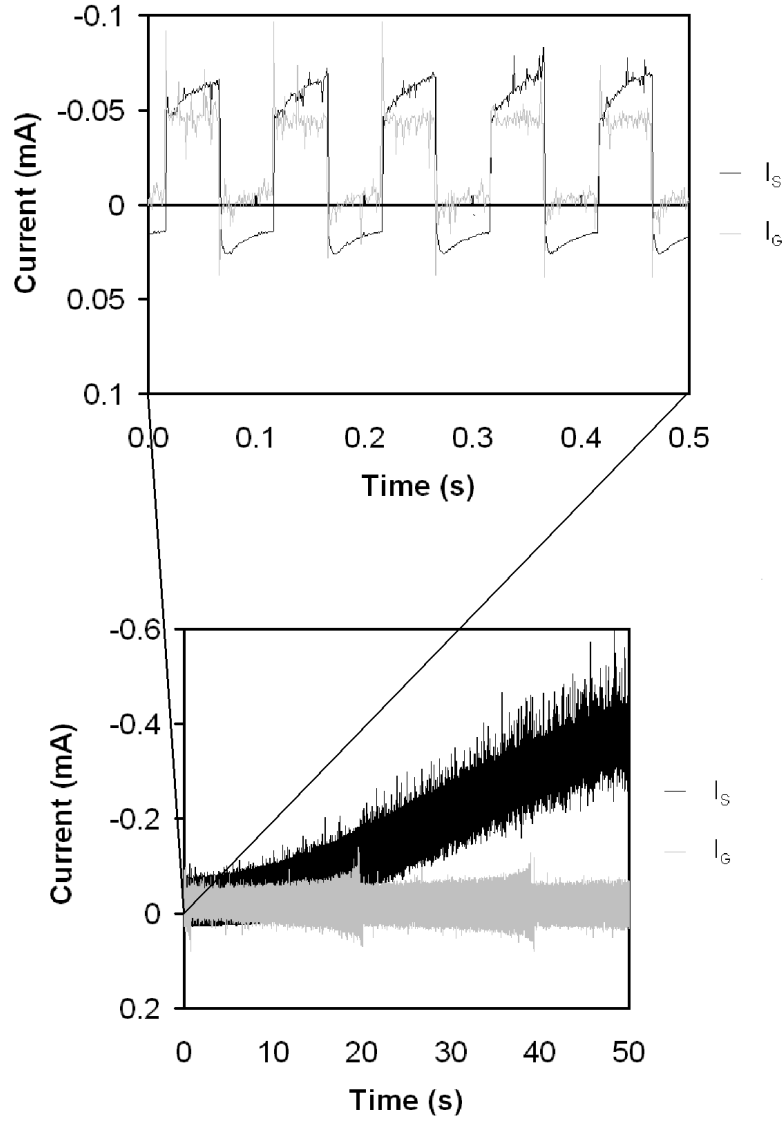


FIGURE 5.7: Current versus time relationship for I_S (black) and I_G (grey) in a PVPy:LiClO₄(0.2 M)- based OTFT. 0 to 50 s. Sampling frequency = 1 kHz. $V_{DS} = -2$ V. V_{GS} switched between 0 V and -2 V. Inset shows a 0.5 s sample of data towards the start of the experiment.

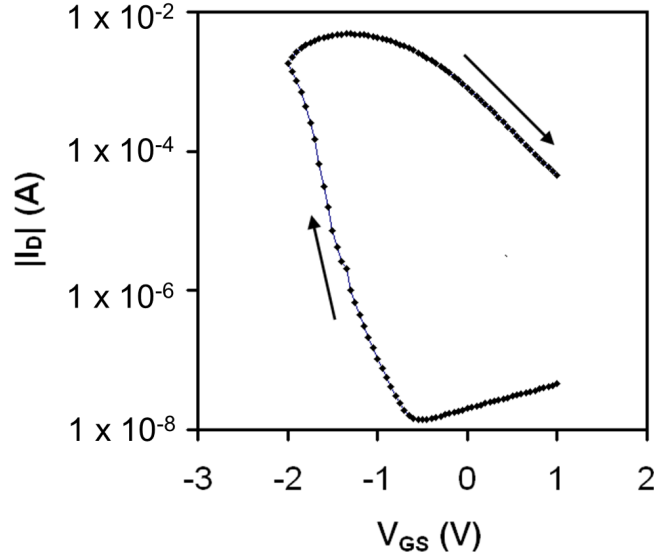


FIGURE 5.8: Transfer characteristic of an OTFT with a PVPy:LiClO₄(0.2 M) dielectric layer. Measured in both directions three times at a scan speed of 25 mV/s. $V_{DS} = -1.5$ V.

Ultimately, in the case of the longer time-scale with the oscillating V_{GS} signal, the relationship of I_S with time is approximately the superposition of the short time scale response with the response of slow response to a single step voltage at the gate. On the other hand, the response of I_G with time stays at the same level. Since I_D is the difference between I_S and I_G , we can say that the slow response is directly contributed by I_D .

Figures 5.8 and 5.9 show direct transfer characteristic measurements made on a LiClO₄-doped PVPy-based OTFT. Both measurements are for $1 \text{ V} \geq V_{GS} \geq -2 \text{ V}$ (on both directions) and V_{DS} at -1.5 V, however they are taken at different scan speeds. The measurement shown in Figure 5.8 has V_{GS} incrementing in 50 mV steps every 2 s, whereas the measurement shown in Figure 5.9 has 100 s between 50 mV increments. In the case of the faster scan rate, full scale current modulation is achieved, although the peak of $|I_D|$ occurs when V_{GS} is incrementing in the positive direction, indicating that the V_{GS} scan rate is too fast for the mechanisms of I_D modulation to equilibrate. Furthermore, I_D does not return to I_{OFF} levels once V_{GS} has returned to -1 V. On the other hand, the transfer curve taken at the slower scan rate rectifies both these issues. Although there is some hysteresis between the two scan directions, I_D returns to the same I_{OFF} level after the scan and I_{ON} is achieved at $V_{GS} = -2 \text{ V}$. The slower transfer curve was repeated three times to confirm the reversibility and reproducibility of the modulation of I_D .

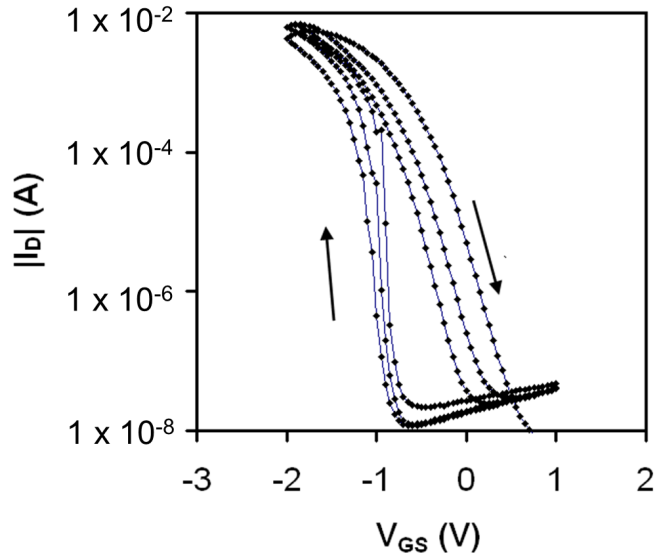


FIGURE 5.9: Transfer characteristic of an OTFT with a PVPy:LiClO₄(0.2 M) dielectric layer. Measured in both directions three times at a scan speed of 0.5 mV/s. $V_{DS} = -1.5$ V.

5.3 Discussion of the Mechanisms in LiClO_4 -doped Devices

From examination of the output characteristics for the doped-PVPy devices (Figure 5.1), they appear to show two distinct stages of current modulation. Firstly, for $0 \text{ V} \geq V_{GS} \geq -0.8 \text{ V}$, the shape of the output characteristics are quite similar for all salt concentrations (with the exception of the 0.5 M device, Figure 5.1(k), as discussed earlier). This similarity between devices shows that any mechanism dependant on salt concentration is not observed for this range of V_{GS} . The output curves for these low V_{GS} vales resemble those of an undoped PVPy device (Figure 4.3, however, in the case of the doped devices, there is an increase in the I_D value at $V_{GS} = -0.8 \text{ V}$ and $V_{DS} = -1.5 \text{ V}$ to an average of $0.632 \mu\text{A}$ (for LiClO_4 concentrations of 0.005 M to 0.2 M) from an I_D of only $0.015 \mu\text{A}$ in the undoped PVPy-based device presented in Figure 4.3 at the same voltages. This increase in I_D is likely due to the increased number of ions present in the dielectric since the current modulation mechanisms in PVPy devices are suspected to be reliant on ionic movement within the device (as discussed in Chapter 4).

The second stage of device behaviour takes place for $-0.8 \text{ V} \geq V_{GS} \geq -2 \text{ V}$. Now, there is a significant increase in current modulation, the extent of which does depend on the level of LiClO_4 doping resulting in a maximum current modulation ratio of more than 100 000 for the 0.2 M LiClO_4 device. A possible model for describing the operation of the devices is detailed in this section.

Figure 5.10(a) illustrates the devices when there is no gate voltage applied; pairs of Li^+ and ClO_4^- ions tend to be attracted to each other due to their opposing electrical charges and are distributed arbitrarily throughout the dielectric layer. For $0 \text{ V} \geq V_{GS} \geq -0.8 \text{ V}$, the potential between gate and source creates an electric field which is sufficient to cause the ion pairs begin to separate and drift towards opposite edges of the dielectric layer (Li^+ towards the PVPy/PEDOT:PSS interface and ClO_4^- towards the P3HT/PVPy interface - Figure 5.10(b)). The layer of anions (ClO_4^-) near the dielectric-semiconductor interface forms a layer of negative charge which in turn increases the conductivity of the source-drain channel resulting in the observed increases in I_D of approximately one order of magnitude. For these smaller values of V_{GS} , the current modulation mechanism could potentially be either electrostatic or electrochemical. However, for values of V_{GS} more negative than -0.8 V , the mechanism which induces a change in I_D of several orders of magnitude is somewhat slow (Figure 5.6), and is therefore suspected to be electrochemical in nature. Bäcklund et al. suggested previously that in their HIFET devices with a PVP dielectric (similar to those examined in Chapter 3) current modulation is caused by anions in the dielectric moving to the P3HT/PVP interface under the influence of V_{GS} and subsequently doping the semiconductor by oxidation [48]. In the salt-doped dielectrics of the devices presented here, a similar mechanism could conceivably be driving the ion-enhanced current modulation for $-0.8 \text{ V} \geq V_{GS} \geq -2 \text{ V}$ (Figure 5.10(c)). The H^+ and OH^- ions

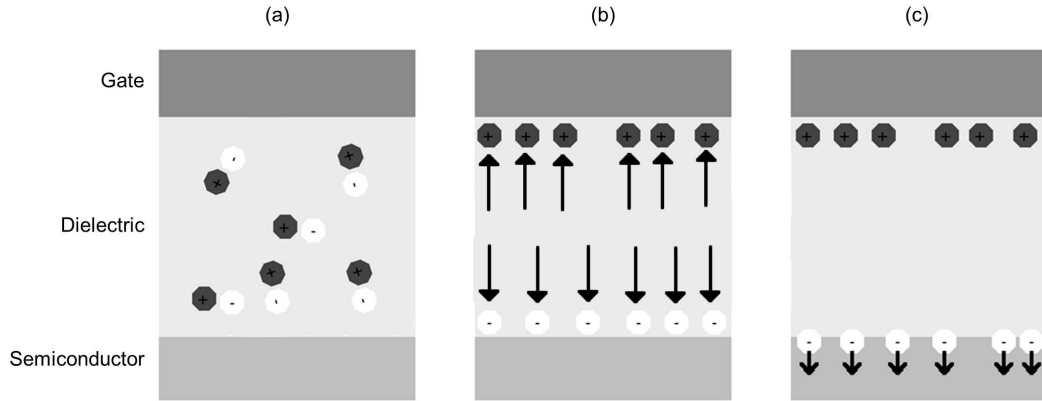


FIGURE 5.10: Simple pictorial description of the movement of the ions introduced into the PVPy dielectric. (a) no voltage applied to any electrode, the anions and cation pairs are randomly distributed; (b), small voltage applied to the gate, ions move to the dielectric interfaces; (c), at a higher level of V_{GS} , the anions begin to electrochemically dope the P3HT layer, increasing its conductivity.

which exist in the device due to the dielectric’s hygroscopic nature (as well as the Li^+ and ClO_4^- ions) could also potentially participate in this process, however the device’s behaviour is dominated by the large current modulation facilitated by the dopant salt.

For a given $V_{GS} \in [-0.8, -2]$, as $|V_{DS}|$ increases and eventually exceeds $|V_{GS}|$, the Li^+ ions become attracted to the drain as well as the gate. This drift of Li^+ then “screens” the P3HT doping effect of ClO_4^- ions at the semiconductor/dielectric interface near the drain, creating two distinct regions of P3HT conductivity in the channel between source and drain: a high-conductivity region near the source electrode still influenced by the anions, and a low-conductivity region nearer to the drain where this doping effect has been reduced. The size of the low-conductivity region increases as V_{DS} becomes more negative, causing the saturation characteristic observed in the output characteristics (equivalent to “pinch-off” in field effect devices - Figure 1.4(d)).

As established earlier, PVPy is hygroscopic in nature and, as such, when the devices are characterised in air the dielectric layer is moisture-rich. We can therefore consider the doped-PVPy dielectric layer as a “quasi-aqueous” solution of ions. It is conceivable that the movement of ions within the dielectric layer could be similar to that of ions in an aqueous solution, and thereby the ions would be surrounded by a “hydration sphere”: a volume of water molecules which are bound to an ion in an aqueous environment, the size of which depends on the charge density of the ion [105]. The idea of the movement of ions being affected by a hydration sphere is examined in

the Section 5.4 where Li^+ is replaced by a cation with a smaller hydrated radius.

However, as stated above, when there is no V_{GS} applied to the devices, it is expected that ions are distributed through the PVPy layer in pairs (similarly to other reported descriptions of ions pairs in aqueous solution [106, 107]). Before the ions separate and become fully hydrated, they are an intimate or internal ion pair within the quasi-solution of the dielectric layer and share solvating water molecules. Thus, since they are not individually fully hydrated, the distance between their centres is not determined by their hydrated radius but their ionic radius. Thus, the minimum distance separating the centres of the ions is the sum of their ionic radii.

According to Coulomb's Law, the force between two charges can be determined as follows:

$$F = \frac{q_1 q_2}{4\pi\epsilon r^2} \quad (5.1)$$

where F is the attractive force between the two ions, q_1 and q_2 are the strength of the charges, ϵ is the permittivity of the separating medium and r is the distance between the centres of the charges. Equation 5.1 can be rewritten as:

$$F = \frac{k}{r^2} \quad (5.2)$$

where k is a constant equal to $q_1 q_2 / 4\pi\epsilon_0$ since r is the only variable which will change as the ions move within the dielectric. From Equation 5.2 it is easy to determine that the force attracting the anions and cations will be stronger if they are closer together. This relationship is discussed further in section 5.4 below.

5.4 Introduction of Sodium Perchlorate as a Dopant

To test the hypothesis of the ions in these OTFTs travelling within the dielectric layer surrounded by a hydration sphere, and to determine if device performance can be tuned and/or enhanced through the use of different ionic dopants, LiClO_4 was replaced with a different salt: sodium perchlorate (NaClO_4). Na^+ is now the dopant cation instead Li^+ . Sodium was chosen to replace lithium due to them being similar materials (both alkali metals), but having different hydration sphere sizes: despite being a physically larger ion, Na^+ actually has a smaller hydration sphere than Li^+ due to its lower charge density. Reported values for ionic radii and hydrated radii of alkali cations vary depending on the measurement technique used [108–110], however the trend of hydrated radii decreasing with increasing ionic radii (as in the values reported in Table 5.1) is consistent. Therefore, it is possible that Na^+ will be more mobile than Li^+ within the devices if the hydration sphere hypothesis is correct. Indeed, the mobility of Na^+ has been already reported as being higher than Li^+ in water [111]. This increase in ion mobility could conceivably manifest itself in terms of device characteristics as a reduction in $|V_{TH}|$ or an increase in I_{ON} , both potentially the result of Na^+ being more

Metal	Ionic Radius (Å)	Hydrated Radius (Å)
Lithium	0.94	3.82
Sodium	1.17	3.58
Potassium	1.49	3.31
Rubidium	1.63	3.29
Caesium	1.86	3.29

TABLE 5.1: Ionic and hydrated radius of some alkali metal cations [110].

easily separated from ClO_4^- than Li^+ due to its smaller hydrated radius. The relative sizes of Na^+ and Li^+ ions (both hydrated and non-hydrated) are shown in Figure 5.11.

With regards to the size of the perchlorate ion, the only set of data in the literature which reports the ionic and hydrated radii of Li^+ , Na^+ and ClO_4^- together was published by Nightingale [108]. Nightingale reports the ionic and hydrated radii of ClO_4^- to be 2.92 Å and 3.38 Å respectively, while the hydrated radii of Li^+ and Na^+ are stated as 3.82 Å and 3.58 Å. This means that although ClO_4^- is more massive than either of the cations and has a larger ionic (non-hydrated) radius, it is smaller than them when hydrated.

Since 0.2 M was the concentration which most effectively enhanced device performance in the LiClO_4 case, the experiments with NaClO_4 as the dopant also used a concentration of 0.2 M in the PVPy-ethanol solution. Figure 5.12 shows the output characteristic of an NaLiO_4 -doped device. This device bears a strong resemblance to the LiClO_4 -doped device of the same dopant concentration (Figure 5.1(j)). If any differentiation can be made between the two output characteristics, the I_{ON} levels in the device with the sodium ions are slightly higher.

Figure 5.13 shows the transfer characteristics of two doped PVPy OTFTs: one doped with LiClO_4 and one doped with NaClO_4 , both at a concentration of 0.2 M. Both devices are representative of a typical device of their type. One can see that the NaClO_4 -doped OTFT turns on at a lower $|V_{GS}|$ than the LiClO_4 -doped devices; that is, it has a lower $|V_{TH}|$ (and hence operating voltage). This observation is consistent with Na^+ being more mobile than Li^+ , supporting the hydration sphere model to describe ionic movement within the dielectric. Furthermore, when the dopants exist as ion pairs in the dielectric (prior to being separated by V_{GS}), Li^+ is more strongly bound to ClO_4^- than Na^+ , which also is supported by the data. In other Na^+ 's larger ionic radius and smaller hydrated radius compared with Li^+ makes it both more easily separated from its anion and more mobile within the dielectric under this model.

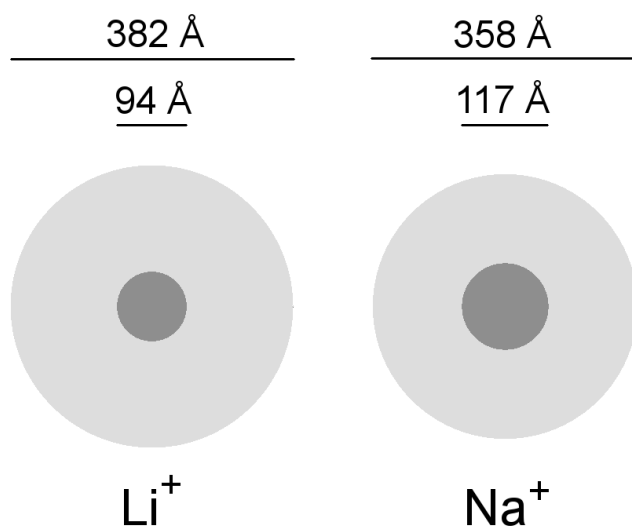


FIGURE 5.11: Diagram showing the relative sizes of the ionic (dark grey) and hydrated (light grey) radii of lithium and sodium ions.

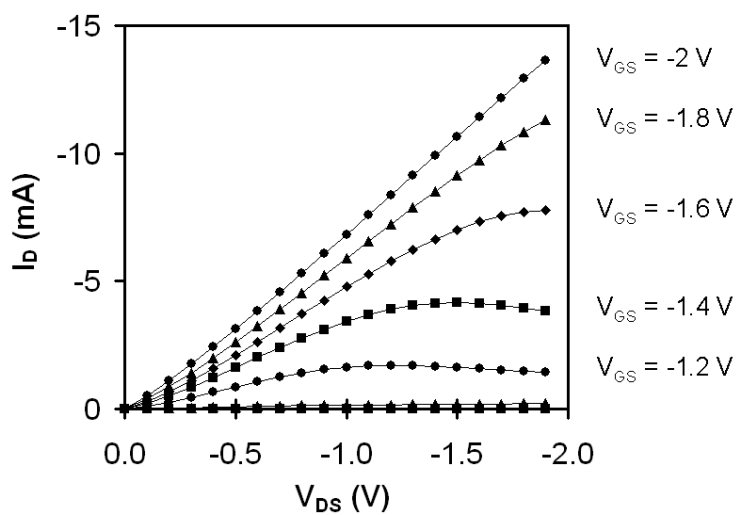


FIGURE 5.12: Output characteristic for an OTFT with a PVPy:NaClO₄(0.2 M) dielectric layer.

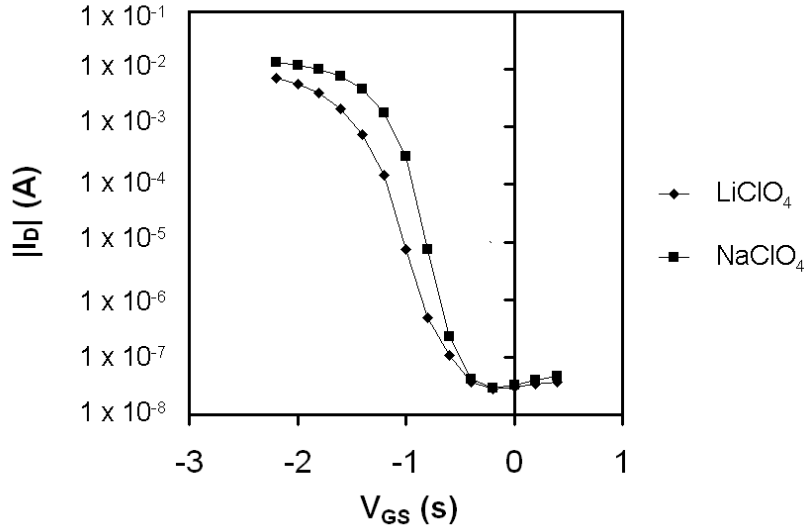


FIGURE 5.13: Transfer curves extracted from output characteristics at $V_{DS} = -1.5$ V for a $\text{LiClO}_4(0.2 \text{ M})$ and $\text{NaClO}_4(0.2 \text{ M})$.

In summary, despite its relatively large physical size compared with Li^+ , Na^+ appears to be more mobile within these doped PVPy-based OTFTs due to a lower observed turn-on voltage. Both the Coulombic attraction between oppositely charged ions and the hydration sphere model for ionic movement within the dielectric layer account for this observation and raises the opportunity for further investigations into other cationic and anionic species for use in ion-doped dielectric layers. The hydration sphere model is applicable to these OTFTs due to the hygroscopic nature of their dielectric layer.

5.5 Conclusion

In this chapter, successful dielectric doping of OTFTs by two salts, LiClO_4 and NaClO_4 , has been presented. The fact that the anions of these salts is common (ClO_4^-) allowed for a direct comparison of the two cations leading to some insights into the device operation: further confirmation of the water-rich state of the dielectric during device operation due to the ions being subject to a hydration sphere when moving within the layer. Furthermore, varying the type of ions in the device appears to be a promising way to selectively modify the electrical properties of the OTFTs. It is expected that introducing other types of ions into the device could provide avenues for further studies in this area. For example, perhaps employing a more mobile anion would be a way to reduce the operation voltage and or transient response of the devices.

From the evidence presented here, it is clear that doping PVPy dielectric layers with salts is an effective method to enhance current modulation in OTFTs. The addition of these salts increases the amount of ions in the system compared with the undoped PVPy- or PVP-based devices. Since the electrochemical mechanism which facilitates the turn on in I_D to levels of over 1 mA in the doped-PVPy dielectric devices is somewhat slow, applications are somewhat limited in the present stage of development. Many transistor applications such as switches in microcontrollers or analog amplifiers require much faster operation. However, the device in this iteration could still be useful in some applications where the response of the device is non-critical, such as for some sensors.

5.5.1 Future Work

The hydration sphere model of ionic transport in the PVPy dielectric layer has the capacity for more extensive verification by the introduction of dopant salts with different cations. For example, the alkali metals appearing in Table 5.1 should show increased mobility (translating in to lower $|V_{TH}|$ values and/or higher current modulation ratios as seen when Li^+ is replaced by Na^+). Also, changing the dopant anion will be an interesting way to more deeply investigate the mechanisms involved.

The main disadvantage of the variety of OTFT presented in this chapter is its relatively slow response to achieve full current modulation. The transient response of current modulation may be limited by the mobility of the dopant ions in the dielectric layer and ease by which electrochemical doping of the P3HT layer can occur. It is expected that there is some optimisation to be achieved in both architecture optimisation and material selection which may be directions for future work.

Eventually, once the device materials and fabrication procedure have been optimised, building elements such as logic gates, as well as designing amplifier circuits which utilise these devices is a major avenue for further studies. The OTFTs presented in this chapter are also ideal candidates for sensing applications due to their low operating voltage and high potential current gain.

6

Organic Thin Film Transistors as a Platform for Biosensor Development

Previously in this thesis, the characteristics of several different types of OTFT have been presented. These OTFTs shared the same structure and the majority of materials, however their dielectric materials (and, hence, their electrical behaviour) varied. It has been clearly demonstrated in this thesis thus far that ionic movement within the hygroscopic dielectric layers of these devices allows for transistor-like electrical characteristics at low voltage levels.

Along with the benefits mentioned earlier such as the expanded fabrication possibilities, potential low cost and distinguishing electrical characteristics of OTFTs, the use of organic materials also allows for the incorporation of materials which would otherwise be infeasible in conventional devices. The low-temperature fabrication procedure makes them ideal candidates for the inclusion of materials which would denature or degrade under the high temperatures used in the fabrication of silicon transistors. An example of the type of material that might be included in devices due to this enhanced compatibility is an enzyme: a protein which can catalyse a specific chemical reaction [112]. In particular, enzymes which can catalyse reactions liberating ions could be employed as recognition elements in OTFT-based sensors. So far in this thesis, the crucial role that the movement of ions plays in the devices' operation has already been established, and it seems reasonable to hypothesise that a change in the quantity of ions present in the dielectric layer of the device will induce a change in I_D for some given bias voltages (V_{DS} and V_{GS}). In this case, an enzymatic reaction which liberates ions in quantities proportional to an analyte would in turn change I_D with some relationship to the analyte, thereby creating a sensor. Figure 6.1 shows the structure of a transistor adapted for sensing glucose which will be discussed in detail later in this chapter.

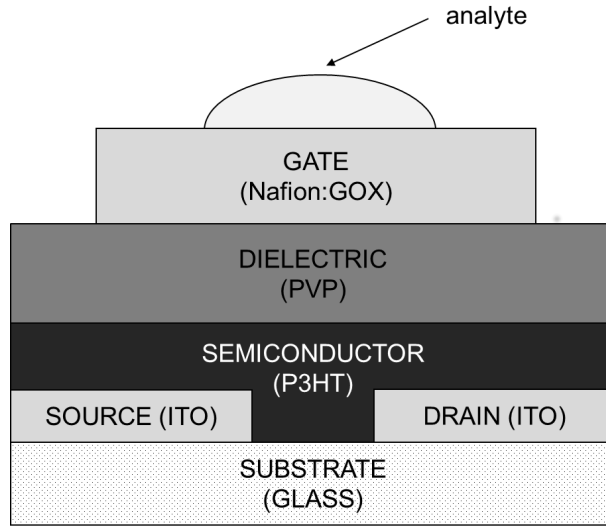
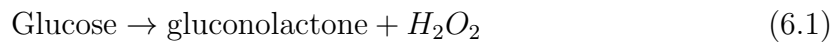


FIGURE 6.1: Device configuration of an OTFT-based sensor showing where the analyte is dropped.

6.1 Glucose Oxidase as a Model Enzyme

Glucose oxidase (GOX) is an enzyme which selectively oxidises glucose according to the following relationship [113] :



(in the presence of GOX and O_2)

This H_2O_2 (hydrogen peroxide) can then be broken down electrochemically according to the following relationship [60]:



(at 0.7 V vs SCE)

These two reactions will in theory generate protons in quantities proportional to an amount of glucose presented to a given quantity of GOX.

In this chapter, OTFT-based enzymatic glucose sensing is conducted with the ultimate aim of achieving sensitivity in the range for glucose concentration in saliva which is generally reported to be 8 to 200 μM [114]. The devices presented look to use GOX to liberate a quantity of H_2O_2 , and hence in turn H^+ , in the device which is proportional to the glucose concentration of an analyte solution presented. It is expected that the

mechanism which would cause a change in I_D when H_2O_2 is broken down and protons are liberated is the same as the mechanism by which the acidic, aqueous PEDOT:PSS solution in the standard OTFTs causes a base level of doping to their P3HT layers (as discussed in Chapter 3). It is known that the PVP dielectric layer freely allows doping of the P3HT by protons in the PEDOT:PSS solution and would likely do so in this case as well. As such, PVP was chosen as the appropriate dielectric material for this study.

The sensing of glucose using GOX in particular is good for the first iteration of a sensor platform because GOX's reaction with glucose is a very well-studied one. Indeed, a wide variety of glucose sensors based on GOX have already been reported. Several studies have been conducted on sensors using GOX as the recognition element in organic devices; however they have the downside of operating at high voltages, involving complex fabrication techniques or require complex external circuitry such as an electrochemical cell [60–62].

Even though there is only one type of enzyme examined here, it is envisaged that this type of OTFT could be a versatile platform for the development of sensors based on enzymatic reactions in general, so long as the reaction liberated ions which could contribute to current modulation.

6.1.1 Social Demand for Glucose Sensing

As was mentioned in Chapter 1, there is a growing demand worldwide for blood glucose sensors due to the increasing prevalence of type 2 diabetes, especially in the western world [58]. With this demand also comes the need, specifically, for non-invasive methods of measuring the concentration of glucose in blood [115, 116]. Currently, many measurement methods require actual samples of blood to be taken from the sufferer which can be painful and socially awkward. Due to the correlation of the concentration of glucose in blood to glucose in saliva, it should be possible to develop a blood glucose sensor which uses saliva as the analyte-containing solution.

6.2 Adapting a Standard OTFT for Enzymatic Sensing

In order to use GOX as the recognition element in an OTFT-based sensor, the enzyme needs to be located in the devices such that it can be readily accessed by (or have access to) the glucose analyte. The obvious position to incorporate it is in the gate layer which is the most exposed part of the device. However, there is a compatibility problem with the existing gate material PEDOT:PSS and the enzyme GOX. GOX loses its activity when it is in low pH environments [117] and the PEDOT:PSS suspension used for the gate in the standard devices has a pH of 1–2. A material is required which

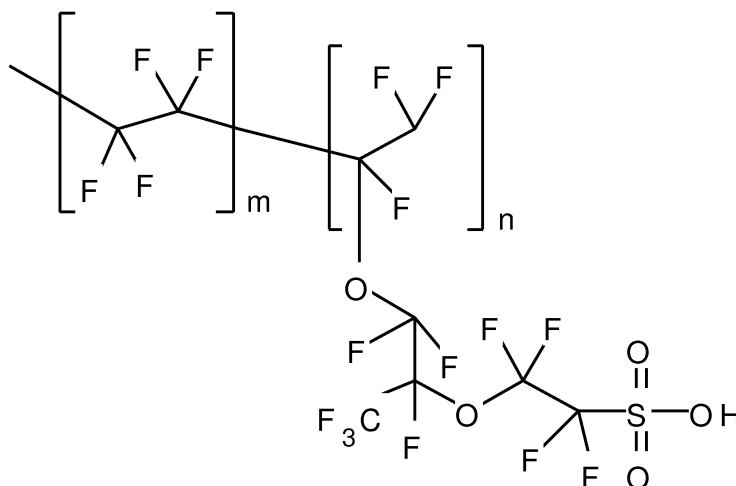


FIGURE 6.2: Chemical structure of Nafion.

will allow GOX to be safely incorporated within it, as well as providing the proton conduction necessary to facilitate transport of the ions liberated from the breakdown of glucose and H_2O_2 .

Nafion (Figure 6.2) is a proton transport membrane which is readily available commercially [118]. The Nafion used in this work was purchased in a solution of mostly propanol and water from Sigma-Aldrich. It has a more neutral pH than the PE-DOT:PSS solution making it more compatible with GOX. Nafion mixed with GOX was implemented as the gate material for the sensing OTFTs discussed in this chapter.

6.3 Summary of Previous Electrochemical Experiments

Research involving the sensing of glucose using GOX embedded in Nafion films has already been conducted in this group, some of which was presented in a Masters thesis by Sirois [119]. The findings of this previous work will be summarised here before the new work is presented. Nafion:GOX films cast on ITO-on-glass substrates were used as working electrodes in a three-terminal electrochemical cell. Solutions of glucose of various concentrations in a phosphate buffer solution were used as the electrolyte in the cell, and cyclic voltammetry (CV) (measuring the current through the counter electrode as a function of the voltage between the working electrode and reference electrode) was conducted.

For CV, the working electrode voltage (V_{WE}) was swept from 0 V to 1 V, then back to 0 V, twice for each concentration of glucose (Figure 6.3(a)). I_{CELL} , which in theory should increase proportionally to glucose concentration upon oxidation of the glucose and the subsequent breakdown of H_2O_2 , was used as the sensing calibration parameter. I_{CELL} at different V_{WE} levels is shown on the calibration curve in Figure 6.3(b). Values of $V_{WE} > 0.9$ V are not represented due to the current levels reaching the limit set for the potentiostat for the higher glucose concentrations. There was a linear trendline fitted to each V_{WE} level, and there was a much better fit to the data (higher R^2 values) for the two highest values: 0.8 V and 0.85 V.

In another experiment, I_{CELL} was coupled to the V_{GS} of an OTFT (similar to the “standard OTFT” as defined in this thesis) via a resistor connected between gate and source (simplified circuit diagram in Figure 6.4). This experiment was designed as a “proof of concept” that a signal which influenced V_{GS} could be used to drive a signal at the output. The device was biased in such a way that changes in I_{CELL} could most effectively modulate I_D and hence V_{OUT} . This experiment also indicated promising potential for OTFT-based sensors.

This previous work, while showing the potential of GOX embedded in Nafion for glucose sensing, has the obvious limitations of requiring external equipment such as the electrochemical cell and the potentiostat which controls it. Furthermore, it requires quite large samples of analyte solution.

The new work presented in this chapter attempts to expand on this earlier work by incorporating Nafion:GOX films into an OTFT in order to have the recognition element as well as signal amplification in the same device.

6.4 Confirming GOX Activity

As a preliminary step in this investigation, it was necessary to confirm the activity of GOX on glucose when it is subjected to the processing steps such drying at temperatures higher than room temperature or simply being exposed to room temperature for prolonged periods. The enzyme is physically fragile and sensitive to temperature (its recommended storage temperature being 20 °C [120]) so there was some concern that it would lose its activity when incorporated into a Nafion film.

In the first experiment of this type, a well was patterned from plastic adhesive tape around the source-drain channel of the standard OTFT substrates. GOX which had been mixed to a concentration of 10 mg/mL in DI water (without Nafion) was dropped into the well and dried at 50 °C. Analytes of plain deionised water (DI water) as well as various concentrations of glucose solution (in DI water) were dropped onto

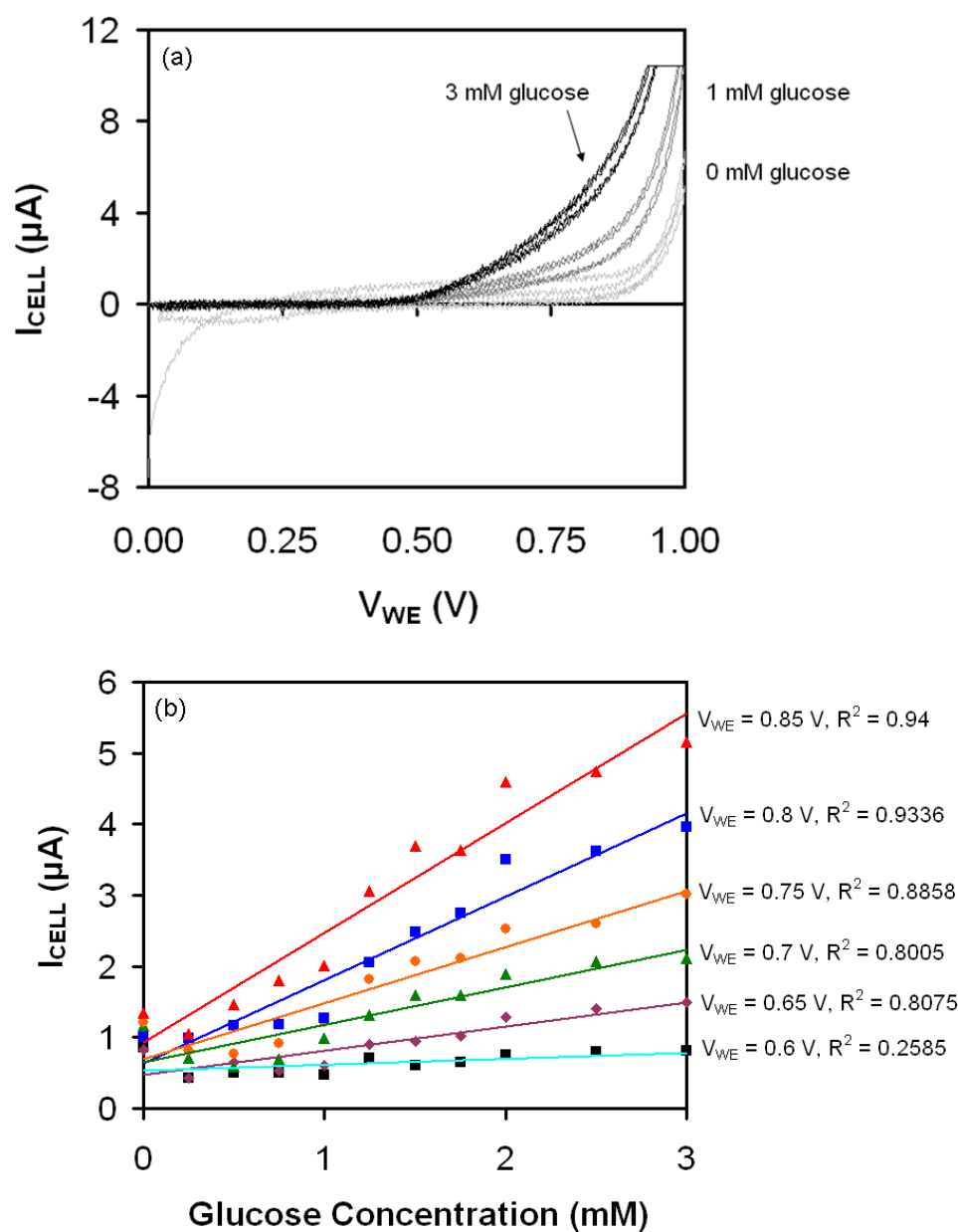


FIGURE 6.3: Sample of previous CV-based glucose sensing. (a) CV plots with electrolyte solutions containing different glucose concentrations: 3 mM (black), 1 mM (dark grey), and 0 mM (light grey); and, (b), the associated calibration curves at different V_{WE} levels. Adapted from data presented in Sirois's Masters thesis [119].

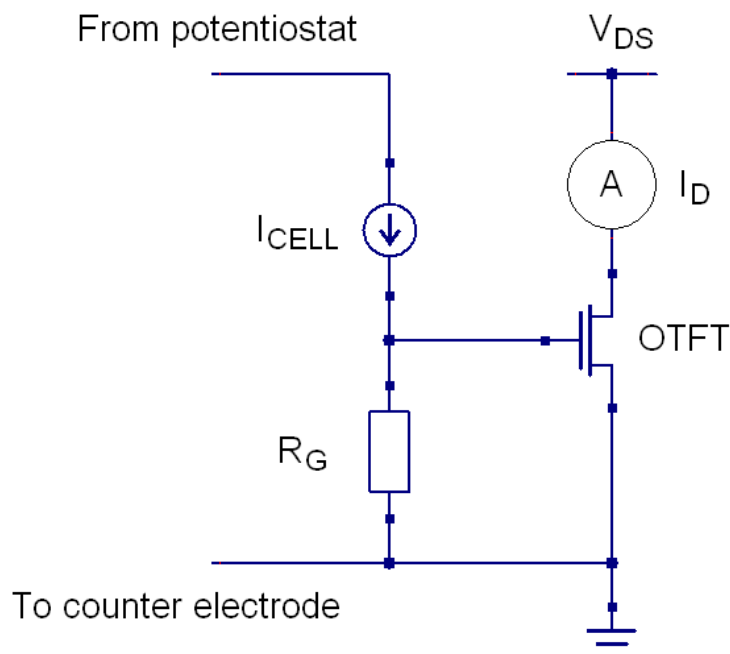


FIGURE 6.4: Circuit diagram of electrochemical cell coupled to an OTFT.

the GOX and the resistance between the source and drain electrodes was measured after 3 minutes. The voltage used by the Keithley SourceMeter 2400 to measure the resistance was not monitored but can be up to 21 V. If there are extra ions in the water between the electrodes due to the breakdown of glucose as described by Equations 6.1 and 6.2, it is expected that there will be a lower resistance in the channel. Furthermore, it is expected that there would be a relationship between this resistance and glucose concentration. In order to confirm that the change in resistance is not due to direct electrochemical action on the glucose, the same experiment was also conducted with no GOX between the electrodes. Figure 6.5 shows the relationship between glucose concentration and resistance with and without the pre-deposition of GOX. Clearly, there is a decrease in resistance with increasing glucose concentration when GOX is present, showing that the activity of the GOX has been retained. With no GOX present, the resistance of the channel shows no relationship to glucose concentration.

Next, it was necessary to confirm the activity of GOX in a Nafion film when an analyte solution was placed on top of the film rather than being immersed in the solution as was the case in the previous work using an electrochemical cell. A simple study was conducted which was similar to the one presented in the previous section where the current between the source and drain ITO pads on a standard OTFT substrate was measured for glucose solutions with and without the presence of GOX. In this case, GOX mixed with Nafion at a concentration of 20 mg/mL, as well as plain Nafion films

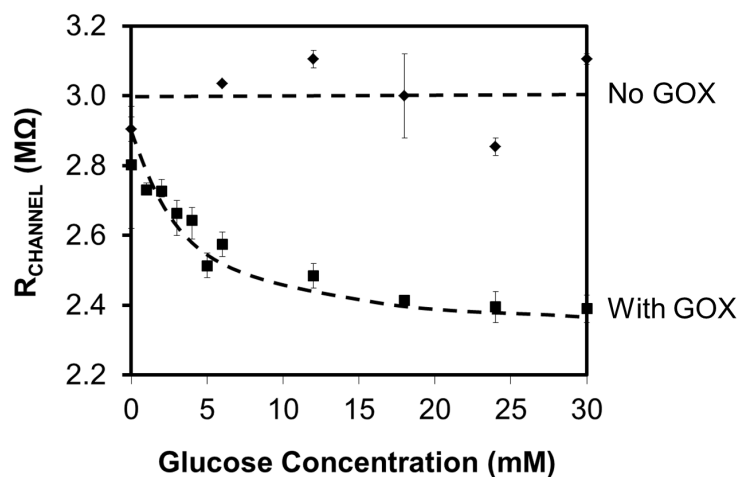


FIGURE 6.5: Resistance between two ITO electrodes (separated by 20 μm across a width of 3 mm) of various glucose concentrations in DI water (10 μL) after 3 minutes. With and without GOX deposited between the electrodes. Trendlines estimated. Measured using ohm-meter mode on Kiethley 2400 Sourcemeeter (voltage up to 21 V).

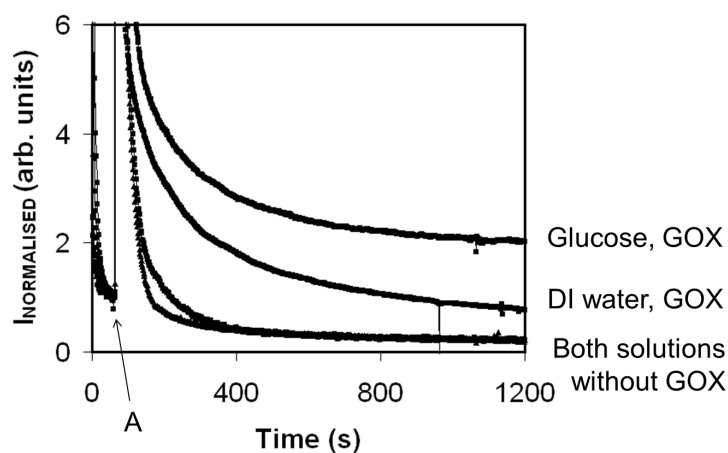


FIGURE 6.6: Change in current with time between two ITO electrode separated by 30 μm at a width of 3 mm connected by a Nafion film (with and without GOX) when exposed to 10 μL of either 30mM glucose solution or DI water. $V = 1\text{ V}$. “A” marks the point of analyte addition.

were drop-cast on substrates on the area above the source-drain channel and allowed to dry at 50 °C. 10 μ L analyte samples of DI water and 30mM glucose in DI water were dropped on top of the device over the channel area. Figure 6.6 shows the current response versus time for this experiment. The disturbance at $t = 100$ s is the addition of the analyte and the currents have been normalised to a ratio of the level prior analyte addition. Clearly, the case with a glucose analyte when GOX is present causes the largest increase in current when is caused by the enzyme activity on glucose and the subsequent production of ions. With no GOX present, there is little difference in the current response between water and the glucose solution.

Devices with this Nafion:GOX gate electrode were also fabricated using the same method as described in the experimental section, only with the Nafion mixture drop-cast as the gate instead of the PEDOT:PSS suspension. GOX was mixed into the Nafion solution at a concentration of 20 mg/mL in the experiments presented below.

6.5 Electrical Characteristics of Sensing OTFT

Figure 6.7 shows the output characteristic of a device with the standard architecture, with the normal PEDOT:PSS gate replaced with a Nafion:GOX gate (as in Figure 6.1). Once again a transistor-like response is observed, with linear and saturation regions, as well as V_{GS} modulation of I_D . However, there are two major changes to the shapes of the output characteristic of a standard device. Firstly, I_{OFF} (at $V_{GS} = 0$ V) is clearly much higher than other types of devices: it is in the order of several microamps. This change results in a lower average current modulation ratio of about 10. Also, there appears to be a linear increase in I_D with V_{DS} for $V_{DS} \leq -1.4$ V, which means that in the saturation region there is still some dependence of I_D on V_{DS} . This behaviour could possibly be explained by current travelling through a path other than the semiconductor: for instance, between source and drain through the Nafion layer. Due to compatibility issues with the PVP solvent (ethanol) and the Nafion solvent (which is a blend of water and some alcohols) it is expected that the PVP/Nafion boundary is somewhat ill-defined, or that the PVP layer is damaged in the area underneath which the Nafion mixture is dropped. Either of these issues could allow for current to flow “around” the P3HT layer if the conductivity of the Nafion and/or the PVP is high enough, effectively creating a resistor in parallel to the transistor, which agrees qualitatively to the shape of the output characteristic curves. The value of this resistance, based on calculations of the slope of the output characteristic curves for $V_{DS} \leq -1.4$ V, is approximately 100 k Ω .

From the transfer curve in Figure 6.8, it can be seen that as well as a reduction in the current modulation ratio of these devices, there is also an increase in their turn-on voltage from $V_{GS} \approx -0.2$ V to $V_{GS} \approx -1.0$ V.

Figure 6.9 shows that the leakage currents for these types of devices are quite low

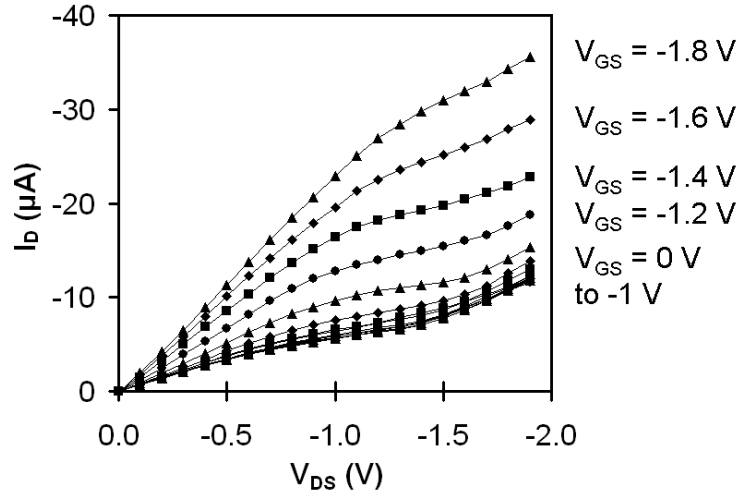


FIGURE 6.7: Output characteristic of an OTFT with a Nafion:GOX gate electrode.

compared with the standard PVP-based device with a PEDOT:PSS gate but not quite as low as the PVPy-based devices.

A study was also carried out to determine the effect of an offset Nafion gate on the device characteristics (similar to some experiments presented in previous chapters with PEDOT:PSS gates). The aim of this was two-fold. Firstly, to determine if Nafion could easily penetrate the PVP dielectric layer and form a conductive path to the source and drain electrodes when it is positioned outside the bounds of the patterned P3HT layer (as is the case with a PEDOT:PSS gate). The second aim was to determine if the “parallel resistor”-style electrical behaviour observed in the output characteristic of Nafion gate devices is due to current flowing from the drain, directly through the Nafion and to the source as was postulated. It was thought that if the gate was deposited such that it intentionally overlapped the area where only PVP separated it from the ITO source and drain electrodes, then it could provide a path for current to readily flow from drain to source or from the gate to another electrode.

Figure 6.10 shows that the output characteristic of the device with the offset gate is somewhat similar to that of the normal Nafion:GOX gate devices: I_{ON} is of the same order of magnitude and the characteristic linear increase in I_D in what would normally be termed the saturation region is still observed. The apparent parallel resistance is still of the same order of magnitude in the offset device and the normal device ($\approx 100 \text{ k}\Omega$). The main difference between the two devices is the increased I_{OFF} level in the offset gate device. However, as Figure 6.11 shows, I_G is approximately the same level as the “normal” Nafion:GOX gate device, indicating that the changes in output

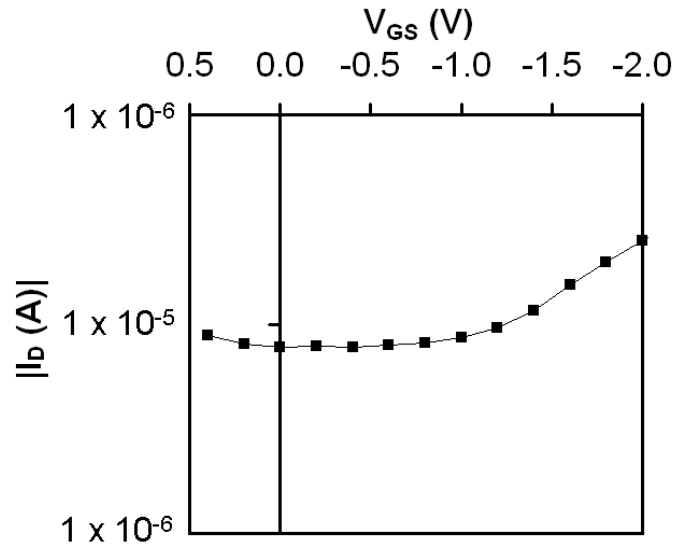


FIGURE 6.8: Transfer curve obtained from output characteristic measurements at $V_{DS} = -1.5$ V of an OTFT with a Nafion:GOX gate electrode.

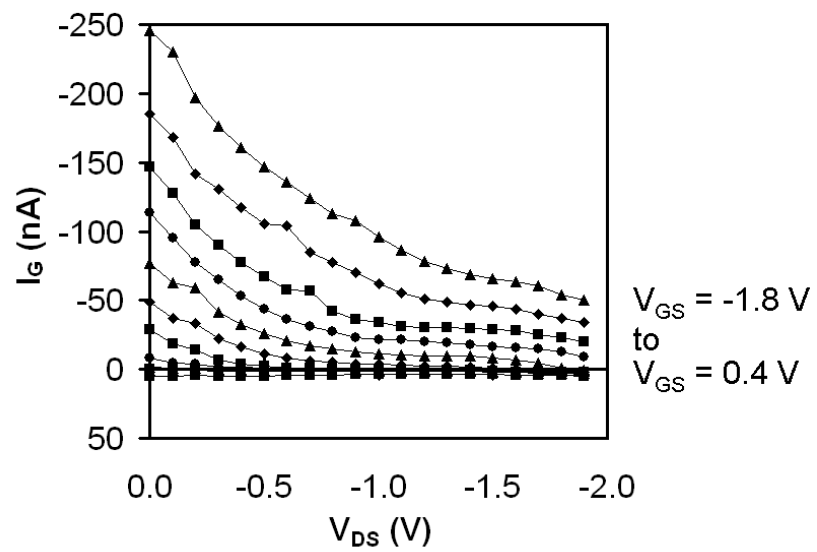


FIGURE 6.9: Leakage currents for an OTFT with a Nafion:GOX gate electrode.

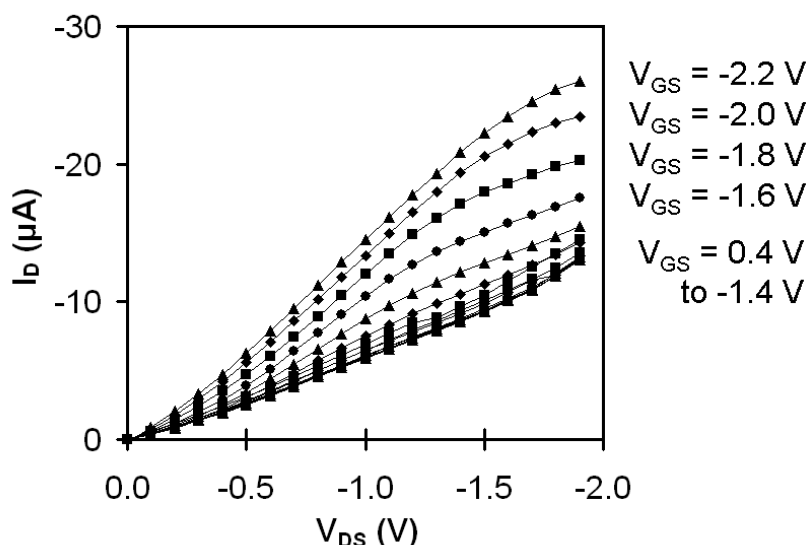


FIGURE 6.10: Output characteristics of OTFT with an offset Nafion:GOX gate.

characteristic are not due to increased leakage currents.

Due to the problems associated with an P3HT/PVP/Nafion:GOX device (poorly defined saturation region, poor current modulation ratio and relatively high turn-on voltage), a PVPy dielectric layer was also considered for use in these sensing OTFTs. PVPy, as observed earlier, forms a more robust film than PVP and may be less susceptible to re-solution and subsequent degradation by the propanol in the Nafion solution. However, because it tends to restrict the movement of protons as shown in Chapter 4, and the enzymatic reaction used for the glucose sensor generates protons which need to modulate I_D , PVPy was not supposed to be the more appropriate dielectric in this case. However, a small pilot study was conducted using PVPy as a dielectric with a Nafion:GOX gate, and the result of this study are presented in Section 6.10. PVP dielectrics will be used in the forthcoming sensing experiments.

6.6 Determining Bias Voltage for Sensor

There are two main factors to consider when choosing the optimal bias voltage levels for the gate and drain in a glucose sensor. Firstly, there needs to be a potential difference between two electrodes in the device which can breakdown the H_2O_2 and liberate protons as per Equation 6.2. This voltage is 0.7 V versus a standard calomel electrode (SCE). Water, on the other hand, is known to undergo electrolysis at 1.229 V [121].

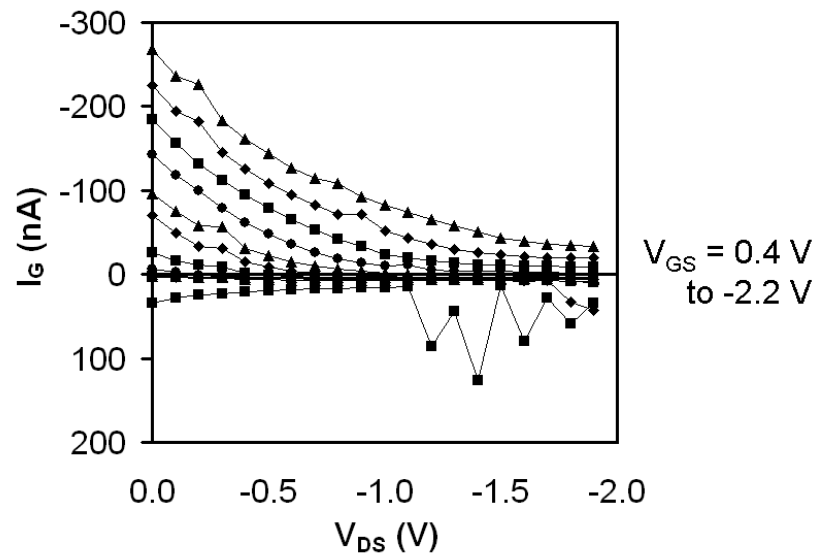


FIGURE 6.11: Leakage current of OTFT with an offset Nafion:GOX gate.

Therefore, care needs to be taken to ensure that a voltage is available in the system to liberate ions from the H_2O_2 without exceeding the potential difference required to cause the breakdown of water which would create an increased background signal.

Although the oxidation potential of water is known, the actual electrode voltages in these devices which causes oxidation may be higher than this depending on voltage drops across the ITO or Nafion, contact resistances and so on, which reduce the actual electrical potentials occurring at the area in the device where this electrochemical process occurs. To determine the V_{DS} level which causes H_2O_2 and water respectively to undergo electrolysis, a simple experiment was conducted. Here, $10\ \mu\text{L}$ samples of various concentrations of H_2O_2 were dropped between the ITO source and drain electrodes of the standard substrates (no other parts of an OTFT were fabricated). The current between the electrodes was measured as “ V_{DS} ” was swept from 0 V to -2 V.

Figure 6.12 shows the results of the experiment described above for a H_2O_2 concentration of 30 mM and for DI water. As can be observed, for V_{DS} more negative than about -0.75 V, the device with the strong H_2O_2 analyte starts to show increased current indicating that the H_2O_2 has started undergoing electrolysis, ions have been liberated and hence the conductivity between source and drain has increased. In the case of the DI water analyte, this process is not observed until the voltage is less than -1.5 V. Therefore, when biasing the device, V_{DS} should be kept in a range between -0.75 V and -1.5 V. There is a discrepancy between the window of appropriate V_{DS} values determined experimentally here, and the theoretical window of 0.7 V to 1.229 V

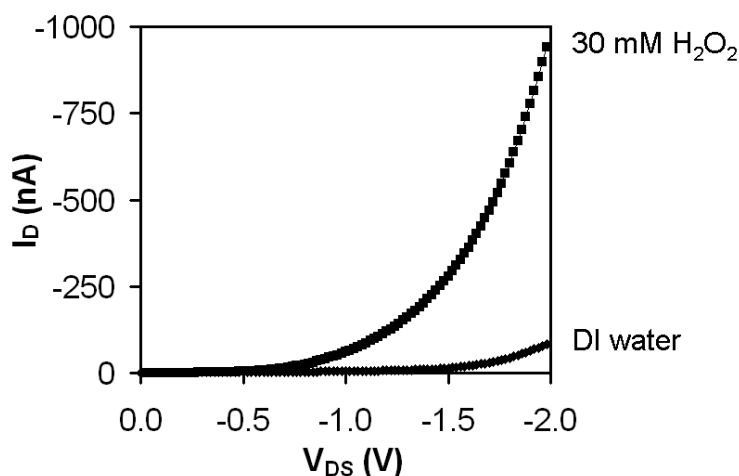


FIGURE 6.12: Current versus V_{DS} for 30 mM H_2O_2 and DI water. This shows the difference in voltages which can break down H_2O_2 and water.

(note that polarity is not considered to be significant here, since $V_{DS} = -1.5 \text{ V} \equiv V_{SD} = 1.5 \text{ V}$). This difference can be attributed to voltage drops occurring across the ITO electrodes and at the ITO/Nafion interface, meaning that $|V_{DS}|$ required for such an oxidation reaction to take place needs to be greater than the theoretical value calculated for an electrochemical cell. For simplicity, V_{DS} will be set at -1 V for subsequent sensing measurements.

The other aspect to consider is the role of V_{GS} and how to bias the gate. Clearly the level of V_{GS} affects the level of I_D , but whether it can take part in the electrochemical reactions in the same way as V_{DS} was unclear. An investigation was conducted in which $10 \mu\text{L}$ of 30 mM H_2O_2 solution was added to two P3HT/PVP/Nafion:GOX devices; one with $V_{GS} = -1 \text{ V}$ and $V_{DS} = -1 \text{ V}$, and the other with $V_{GS} = -1 \text{ V}$ and $V_{DS} = -0.5 \text{ V}$. In this case, the voltage required to ionise the H_2O_2 would not be present between source and drain when $V_{DS} = -0.5 \text{ V}$, but due to V_{GS} being -1 V , it would be available if V_{GS} can carry out this reaction. Figure 6.13 shows that the device biased with $V_{DS} = -0.5 \text{ V}$ does not show the increase in current after analyte addition that the device with $V_{DS} = -1 \text{ V}$ shows. Therefore, it seems that V_{GS} cannot be used to ionise H_2O_2 . However, V_{GS} presumably still plays some part in assisting to move ions within the device. In the following sensing experiments, V_{GS} is set at -1 V .

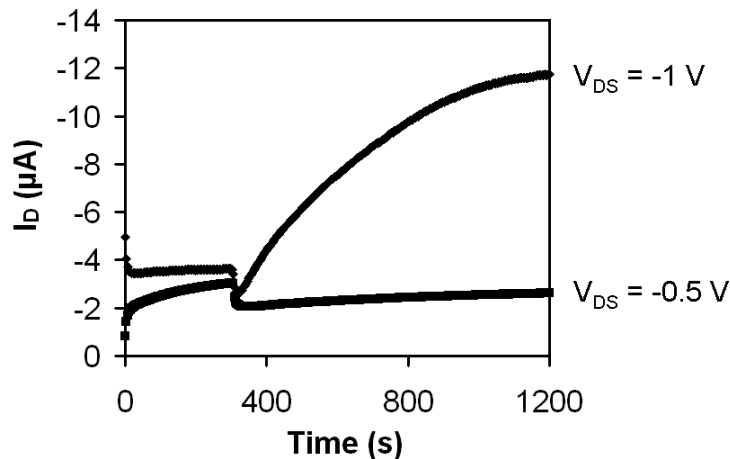


FIGURE 6.13: Response of OTFT-based sensors both with $V_{GS} = -1$ V but having two different V_{DS} values to a 30mM H_2O_2 solution.

6.7 Accounting for Data Variance

When using the change in I_D of these OTFTs as a way to determine the concentration of an analyte in a solution which is dropped onto the device (see Figure 6.1 for the location of the analyte addition), one would ideally desire the same response by any device to any given analyte concentration. If this was the case, by analysing the response of the device it would be trivial to determine the concentration of analyte in the solution. However, the relationship between glucose concentration and I_D response is not so robust in practice. Certain parameters have an effect on the devices which may limit their ability to perform well and to have a consistent response over all concentrations of analyte. These potential limitations will be discussed here.

It stands to reason that there will be some upper and lower bounds to the concentration of glucose (or H_2O_2) which can be detected. The level of I_D will likely reach saturation at some high concentration, and below a certain lower limit, the solution will be indistinguishable from a blank solution (that is, the signal-to-noise ratio will be too low). Such upper and lower bounds exist for any sensor.

The inconsistency in device response and the variance in the initial I_D levels (prior to analyte deposition) of the sensing OTFTs are well illustrated by Figure 6.14, which shows the response to a blank analyte (deionised water only) of seven different devices with each data set measured on a different day, using the same materials and fabrication procedure. The first observation which can be made is that prior to the addition of the solution ($t < 300$ s), both the level of I_D , as well as the relationship between

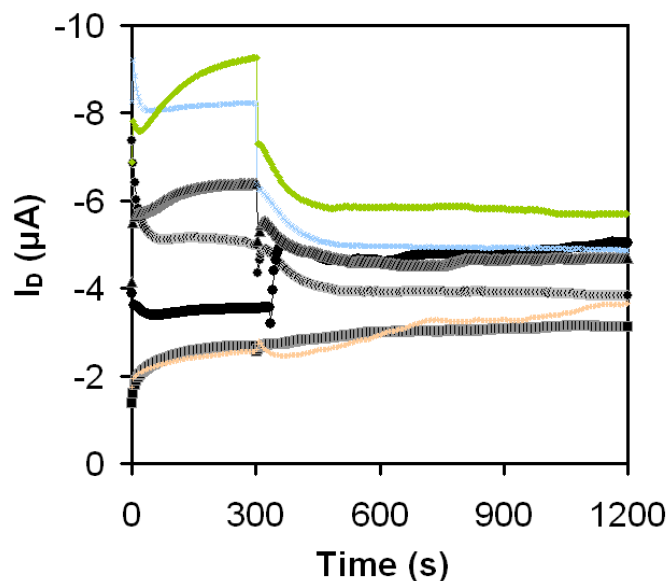


FIGURE 6.14: Response of six different OTFT-based glucose sensors to 10 μL analyte of DI water (raw data).

I_D and time, changes significantly between devices. Then, after adding the water, the response is also inconsistent.

The factors which cause variation in the characteristics of OTFTs with hygroscopic insulators in general, such as temperature and humidity (as mentioned earlier) and device fabrication-related variations as discussed in previous chapters, all likely lead to the inconsistencies observed in the P3HT/PVP/Nafion:GOX devices. In an attempt to account for this variance, and to enable comparison of devices made at different times under different conditions, various normalisation techniques were applied to the data collected during glucose sensing experiments (Sections 6.8 and 6.9). These normalisation methods will be introduced as they arise.

6.8 Response to a Hydrogen Peroxide Analyte

From the experiments conducted in Section 6.6, it is clear that when H_2O_2 is used as the analyte and dropped onto the device, an increase in current between source and drain can be induced when $V_{DS} = -1$ V due to its electrochemical breakdown. Before progressing to glucose sensing and trying to determine a relationship between any change in current and the amount (or concentration) of glucose added, it is sensible, as an intermediate step, to try to determine a relationship with H_2O_2 . Firstly,

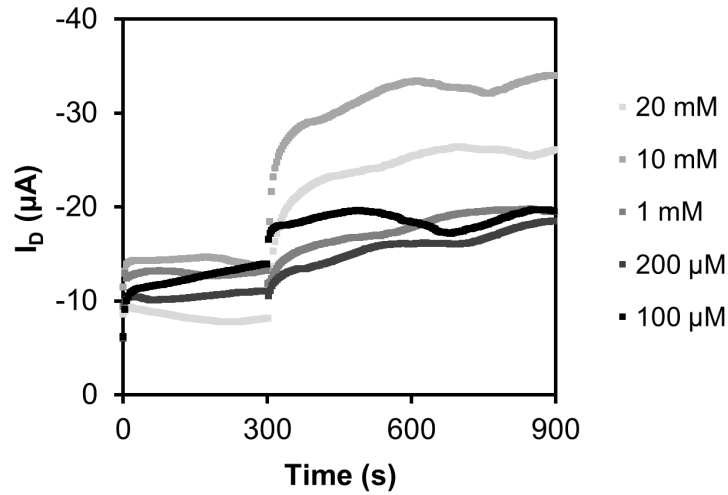


FIGURE 6.15: Raw I_D versus time graphs for five concentrations of H_2O_2 dropped onto OTFTs.

it will give an indication as to the concentrations of glucose which will eventually be able to be detected, since by Equation 6.1, it should be possible to liberate up to one H_2O_2 molecule for each glucose molecule. Secondly, the response to H_2O_2 provides an interesting comparison with the glucose response to identify any lag in the enzymatic reaction and provide some separation from the oxidation of glucose to the breakdown of H_2O_2 .

When measuring the response of these devices to different H_2O_2 concentrations, the analyte solution was introduced to the system simply by dropping it onto the GOX:Nafion layer in the area above the source-drain channel (as in Figure 6.1). The devices were biased at $V_{DS} = V_{GS} = -1$ V, and $10\ \mu\text{L}$ of analyte solution was dropped onto the device whilst I_D was measured as a function of time for 900 seconds. Bias voltages were applied and measurement of current levels began 300 seconds prior to the addition of the analyte.

Figure 6.15 shows samples of raw collected from additions of five different H_2O_2 concentrations to five different OTFTs. It can be easily observed that at $t \approx 300$ s when the analyte solution is added, there is a sudden change in current level. Also, the currents for the two highest concentrations appear to have increased by the largest amount as expected. However, there are significant inter-device variations in the I_D levels before the analyte is introduced ($t < 300$ s) where ideally all devices would behave similarly. Such variations are due to effects such as differing temperature and humidity (neither of which are controlled) both of which can effect the characteristics of these types of OTFTs (as discussed in previous chapters), as well as physical variations in the fabrication process.

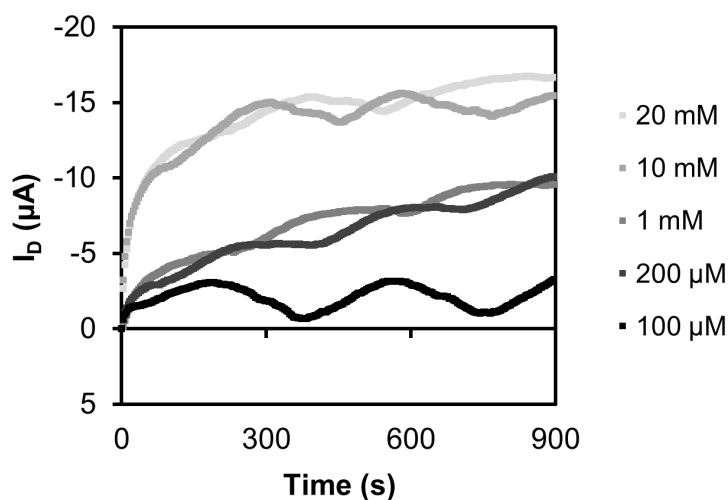


FIGURE 6.16: I_D versus time graphs for five concentrations of H_2O_2 dropped onto OTFTs normalised by subtraction of the current level immediately after analyte addition.

In order to reduce the effects of this variation on our results, some form of normalisation is necessary to compare data sets. Figure 6.16 shows the same data presented in Figure 6.15, except that I_D has been normalised by subtraction from the time immediately after analyte addition, and the data prior to this has not been included. The two strongest concentrations (20 mM and 10 mM) show almost the same response and a larger current increase than the others, the 1 mM and 200 μM responses are also quite similar, whilst the 100 μM analyte induces the lowest increase in current. In this case, the correlation between H_2O_2 concentration and the change in current is more easily observed, although the similarity between the 20 mM and 10 mM responses, as well as the 1 mM and 200 μM responses mean that the increase is not linear with H_2O_2 concentration.

However, simple subtraction is not the only way, and not necessarily the best way, to determine the amount of response by a device to an analyte. Other potential methods for normalising the data could be the subtraction of a background current (where no analyte addition has been made) or by normalising I_D to a ratio of the current before the analyte has been added. Another method is to fit a mathematical function to the trace of I_D versus time and use a co-efficient from the fitted function as the calibration parameter. Upon a visual inspection of the responses of current versus time after analyte addition, I_D appears to rise relatively rapidly immediately following analyte addition before settling to a relatively constant value about approximately 200 to 500 s depending on the device, with the relationship being more clearly defined with the

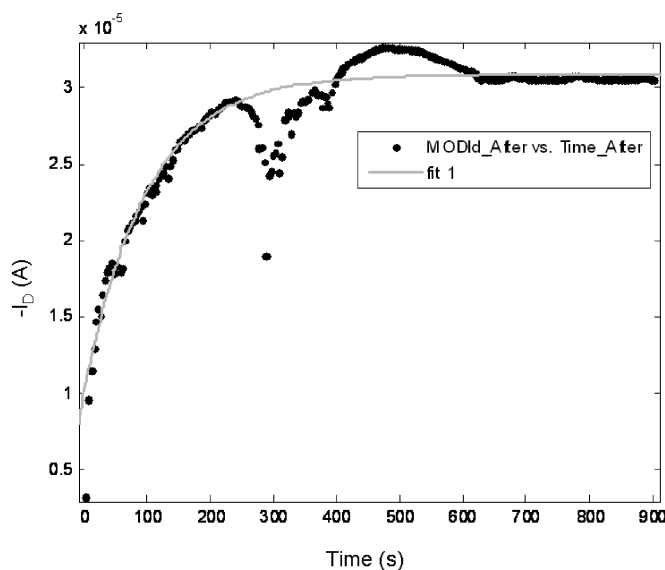


FIGURE 6.17: Example of fitting a function of the form $I(t) = A(1 - Be^{-Ct})$ to the response to 10 μL of 30mM H_2O_2 solution. Only the signal after the analyte is added is considered.

stronger H_2O_2 solutions. A simple equation which fits this type of response is:

$$-I_D(t) = A(1 - Be^{-Ct}) \quad (6.3)$$

where A is the final value of current (at $t = \infty$), $A(1 - B)$ is the value of current immediately following analyte addition and C determines the rate of change of current.

Figure 6.17 shows an example of how curve fitting using the form shown in Equation 6.3, in this instance to a 30 mM H_2O_2 analyte. In Equation 6.3, the coefficient C determines the rate of change of I_D after the analyte has been dropped on the device. If the impedance between the source and drain electrode was modelled as an RC circuit, and the resistance between source and drain changes upon the addition of the analyte solution, then the time constant of the network would also change and this would affect the rate at which I_D changes. If the ions liberated by the breakdown of H_2O_2 are doping the P3HT layer, higher analyte concentrations would lead to lower resistance between source and drain, thereby reducing the time constant. Using this model, C could possibly be used as a calibration parameter to relate the device response to the H_2O_2 concentration.

Figure 6.18 shows a clear relationship between the coefficient C and the H_2O_2 concentration for a given set of H_2O_2 data including in the important range lower than 200 μM . Although there is still a degree of variance in the trend, probably due to device-to-device variations, this method for extracting a calibration curve seems promising.

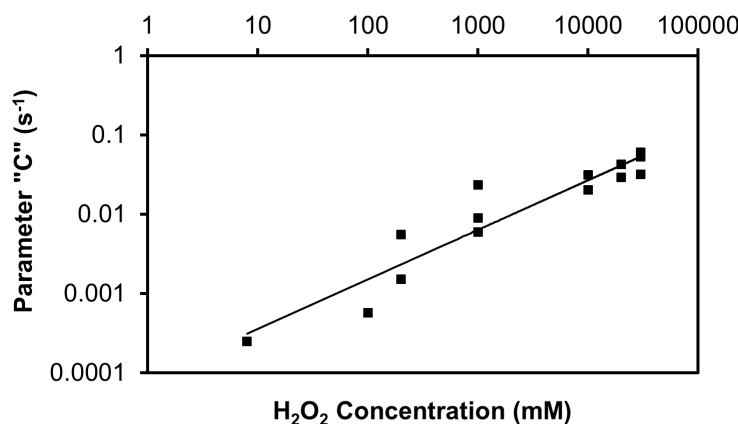


FIGURE 6.18: The parameter C (in the equation $I(t) = A(1 - Be^{-Ct})$) fitted to the current versus time response of glucose analyte dropped onto an OTFT-based glucose sensor versus H_2O_2 concentration. The equation of the trendline is $C = 9 \times 10^{-5} [\text{conc}]^{0.6246}$.

6.9 Response to a Glucose Analyte

In the same way that H_2O_2 solutions were dropped onto OTFTs as analytes, glucose solutions of a similar range of concentrations were also introduced and the response to them was measured. Aside from changing the analyte from H_2O_2 to glucose, the experiments were conducted in the same fashion at the same bias voltages as the previous experiments.

To highlight the difference in the way I_D changes to glucose and H_2O_2 analytes, Figure 6.19 shows the raw (un-normalised) response to three different solutions: 30 mM H_2O_2 , 30 mM glucose and de-ionised water. This clearly shows that, although the glucose solution also induces an increase in I_D , there is a lag in its response compared with the H_2O_2 case. This delay can be attributed to the additive effect of the time taken for glucose within the drop sitting on top of the device to diffuse to a site in the Nafion gate containing GOX, as well as the time taken for the necessary enzyme-assisted reactions to complete, and the liberated protons to migrate to and dope the P3HT layer.

As with the H_2O_2 experiments, normalisation was necessary in order to allow comparison of the response to analyte addition from one device to the next. This was again conducted initially simply by subtraction. However, this time, the currents were subtracted from the level of I_D some time after the analyte addition, once any short term current changes caused by the mechanics of the addition were complete, rather than immediately afterwards as was the case for the H_2O_2 data presented earlier. This point in time is defined in the data presented henceforth as $t = 0^+$ s, and is between 0 s and 100 s after the analyte addition. This delay is included to eliminate any changes in

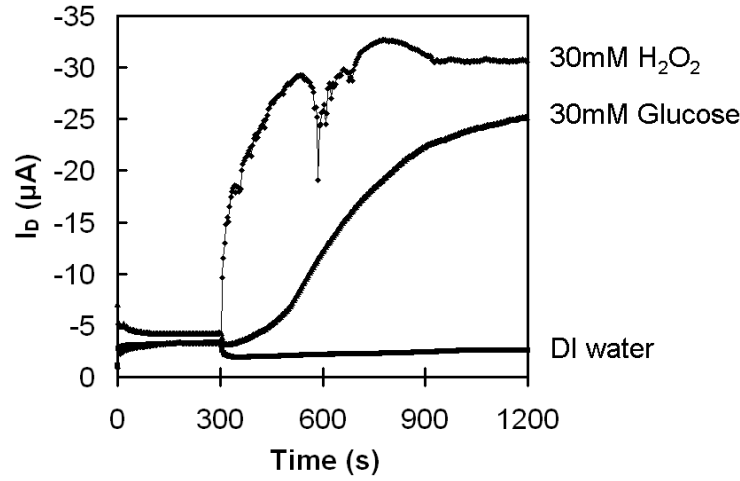


FIGURE 6.19: Current response versus time for water, 30 mM H_2O_2 and 30 mM glucose analytes (raw data).

I_D immediately proceeding analyte addition which was observed in some data sets but seemingly not related to the concentration of the analyte (probably due to the aqueous solution disturbing the existing water in the hygroscopic PVP layer). The slow nature of the response to glucose compared with H_2O_2 (Figure 6.19) means that removing this first part of the data should not be damaging to its integrity.

Figure 6.20 shows I_D as a function of time for four different concentrations of glucose in aqueous solution as the analyte. There is clearly a larger increase in current for the higher glucose concentrations as expected. This data is taken from experiments performed on the same day so that variations in device response due to temperature, humidity and fabrication conditions were minimised.

Figure 6.21, Figure 6.22 and Figure 6.23 show calibration curves for glucose concentration using the difference between I_D at for 3 different time intervals after $t = 0^+$ s: 100 s, 400 s and 800 s. In each case, a trend of larger increases in current with higher glucose concentrations can be observed. Furthermore, as expected, the relationship between glucose concentration and the change in I_D is more well defined after 400 s and 800 s than after 100 s, which confirms that the enzyme-assisted reaction, and hence the response to a glucose analyte, takes some significant amount of time to complete and contribute to current modulation (as indicated by Figure 6.19). However, there is a large level of variance in the results, especially in the range where sensitivity is desired for detecting glucose levels in saliva (lower than $200 \mu\text{M}$). Furthermore, as expected, the relationship between glucose concentration and the change in I_D is more well defined after 800 s than 100 s. Although these calibration curves lack definition for the lower concentrations of glucose, there is a clear trend of increased change in

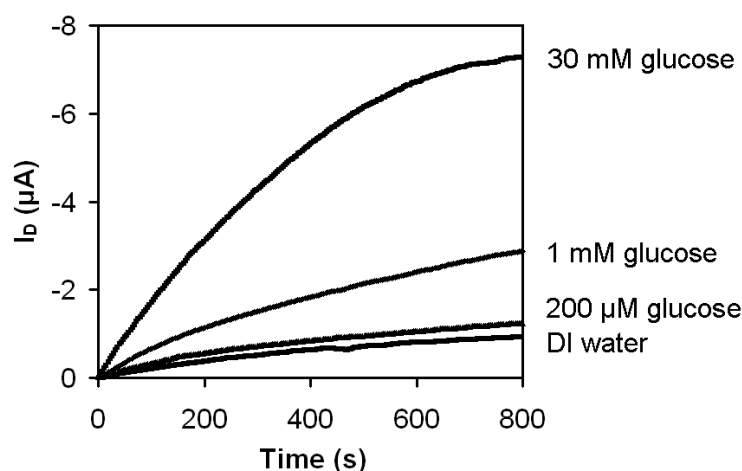


FIGURE 6.20: Current response versus time for 4 different glucose concentrations (conducted on the same day, normalised to the same level 100 seconds after analyte addition).

current with increased glucose concentration which makes for a promising introduction to enzyme-based sensing in the OTFTs.

One way to attempt to improve the calibration curve would be to take the change in I_D over the first 800 s after analyte addition (i.e. the data shown in Figure 6.23), and present it as a ratio of the current level at $t = 0^+$ s. In this way, it was hoped that the effect of the difference in the base conductivity levels of the devices could be reduced on the calibration curve. This plot is shown in Figure 6.24. Although once again there is a clear increasing trend of this parameter with glucose concentration, the variance has not been noticeably reduced.

Another normalisation approach would be to integrate the area under the I_D versus time graph over a certain time period and use this result as the calibration parameter. This method has the advantage of minimising the impact of short term variations in current which might arise from normalisation techniques involving subtraction at two discrete points in time (some of the data already presented here shows that there are short term variations in the I_D versus time plots which do not appear to be related to the concentration of the analyte). Figure 6.25 shows the relationship between the integral of I_D from $t = 0^+$ s to $t = 800$ s and glucose concentration, and Figure 6.26 shows the same parameter as a ratio of I_D at $t = 0^+$ s. When performing the integration, I_D at $t = 0^+$ s is taken to be the baseline of the integral, and is subtracted from each I_D value. When the integral is presented as a ratio of the initial current, some definition in the calibration curve seems to be lost, indicating that the change in current is not

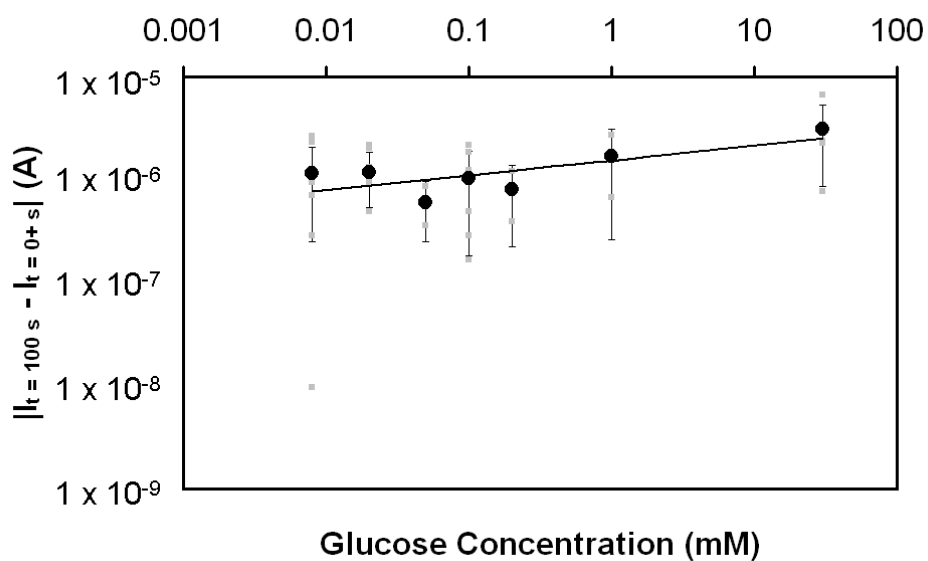


FIGURE 6.21: Calibration curve for glucose using the change in current between $t = 100$ s (after analyte addition) and $t = 0^+$ s as the calibration parameter. Grey dots show the data points, black dots show the average $\pm \sigma$.

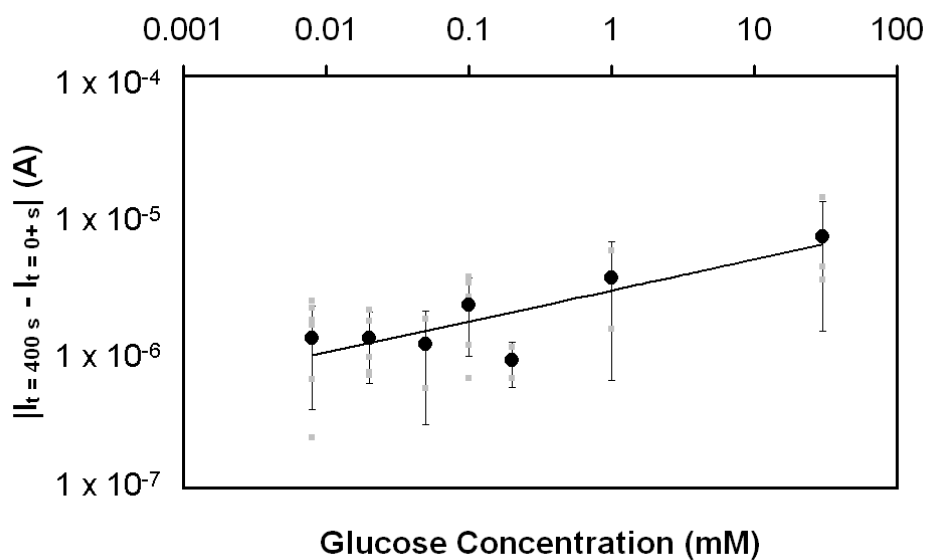


FIGURE 6.22: Calibration curve for glucose using the change in current between $t = 400$ s (after analyte addition) and $t = 0^+$ s as the calibration parameter. Grey dots show the data points, black dots show the average $\pm \sigma$.

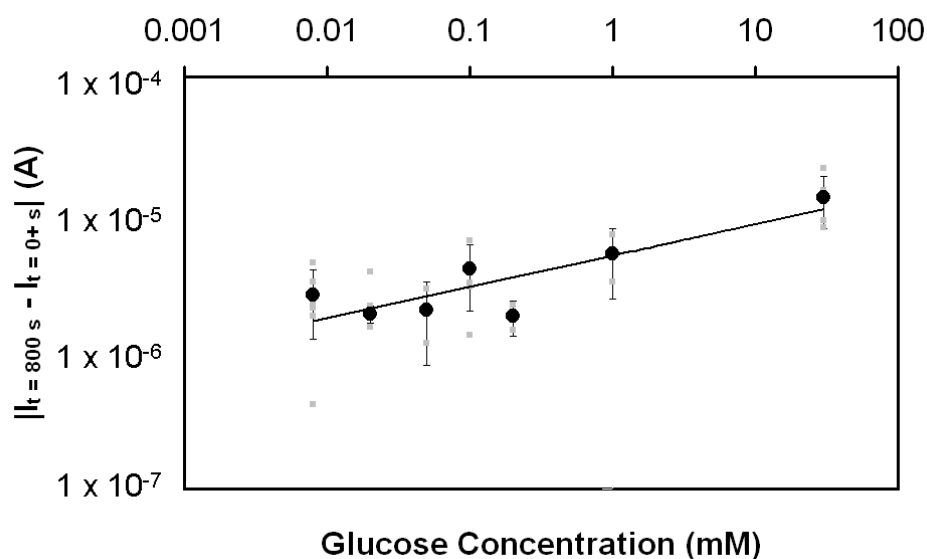


FIGURE 6.23: Calibration curve for glucose using the change in current between $t = 800$ s (after analyte addition) and $t = 0^+$ s as the calibration parameter. Grey dots show the data points, black dots show the average $\pm \sigma$.

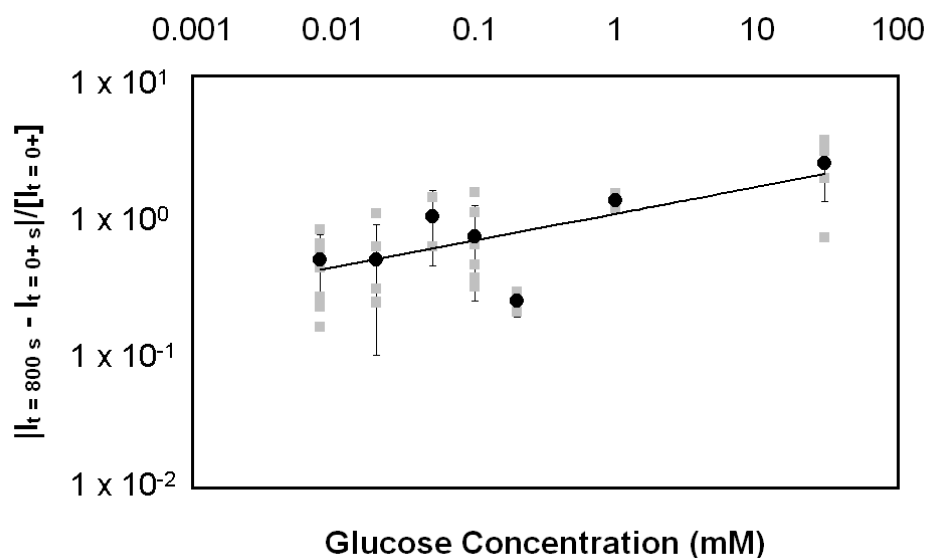


FIGURE 6.24: Calibration curve for glucose using the change in current between $t = 800$ s (after analyte addition) and $t = 0^+$ s as a ratio of the current at $t = 0^+$ s as the calibration parameter. Grey dots show the data points, black dots show the average $\pm \sigma$.

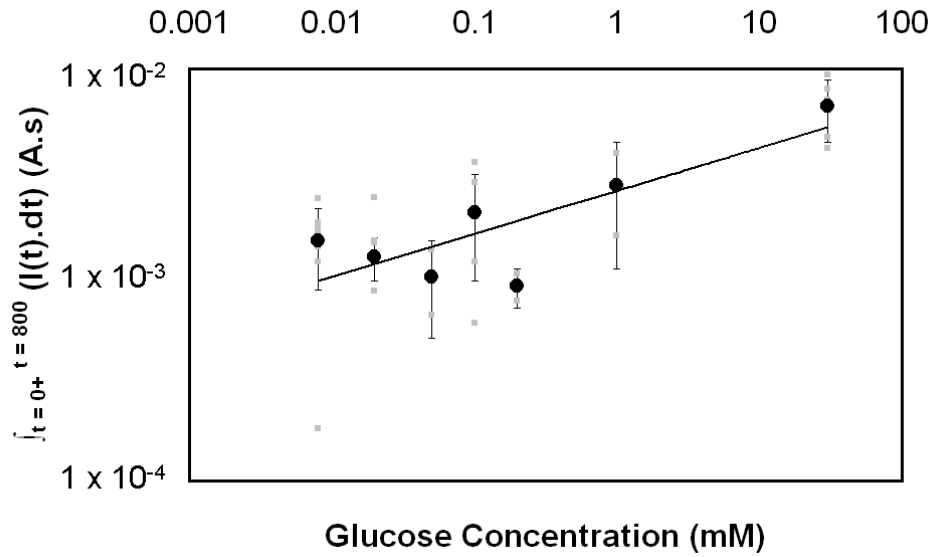


FIGURE 6.25: Calibration curve for glucose using the integral from $t = 0^+$ s to $t = 800$ s as the calibration parameter. Grey dots show the data points, black dots show the average $\pm \sigma$.

necessarily proportional to the initial conductivity of the channel. In a similar fashion to the subtractive normalisation method, whilst the high level of variance (especially at lower concentrations) would prevent reliable glucose concentration detection using these methods, there does appear to be a clear relationship between the parameter and glucose concentration.

Although a curve fitting technique was employed when trying to extract a calibration curve for H_2O_2 , from Figure 6.19 it is clear that the I_D response to glucose is more complex than the H_2O_2 response due to the additional step of the enzymatic reaction which must occur before H_2O_2 can be ionised by V_{DS} . Choosing an appropriate function to fit to the glucose response is therefore considerably more complicated than the H_2O_2 and is not covered in this work. To illustrate the difference in fitting Equation 6.3 to the glucose data compared with the hydrogen peroxide data (which showed a good correlation between concentration and the parameter C which relates to the rate of change of current), Figure 6.27 shows the relationship between C and glucose concentration. Clearly, there appears to be no correlation between glucose concentration and C , so the calibration and normalisation methods presented previously for glucose are much more appropriate. Investigating a better fitting function or otherwise separating the change in signal generated by the enzymatic reaction could be avenues for future investigations.

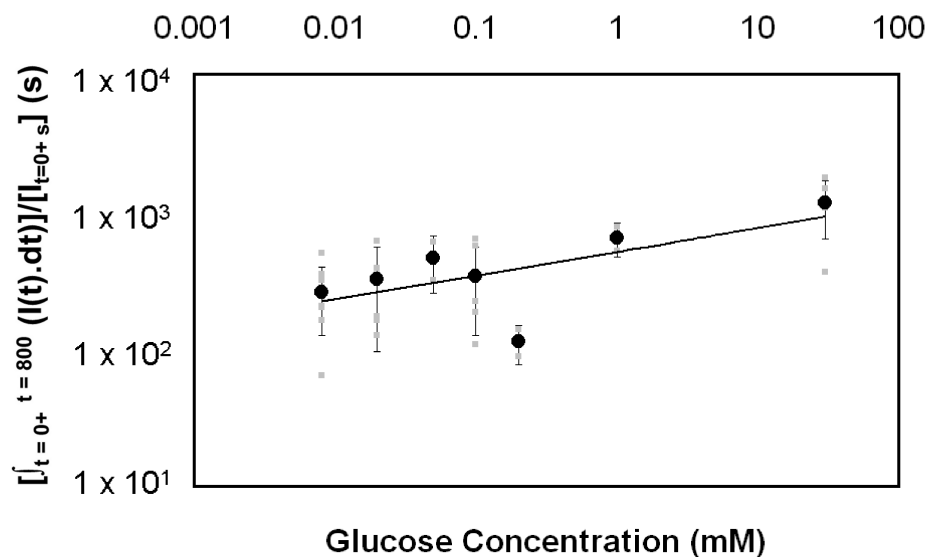


FIGURE 6.26: Calibration curve for glucose using the integral from $t = 0^+$ s to $t = 800$ s as a ratio of the current at $t = 0^+$ s as the calibration parameter. Grey dots show the data points, black dots show the average $\pm \sigma$.

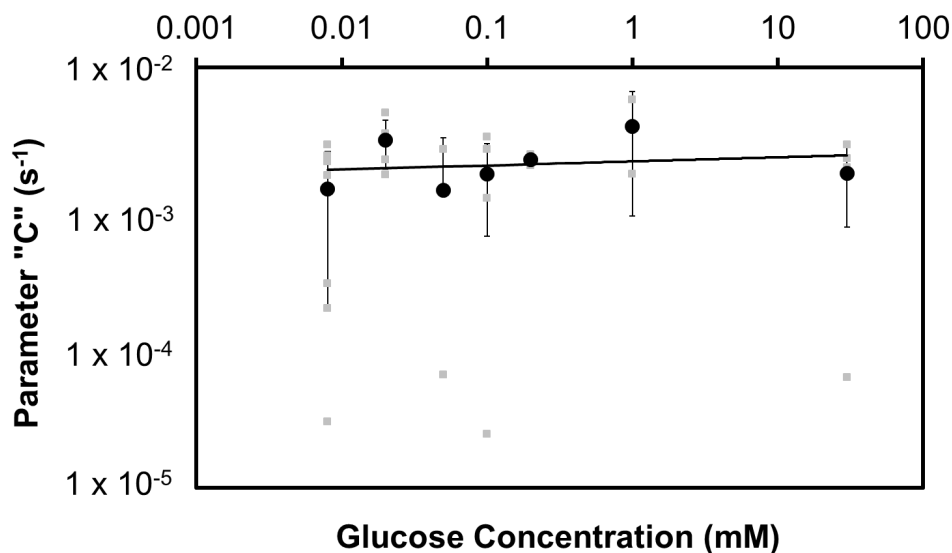


FIGURE 6.27: The parameter C (in the equation $I(t) = A(1 - Be^{-Ct})$ fitted to the current versus time response of glucose analyte dropped onto an OTFT-based glucose sensor versus glucose concentration. Grey dots show the data points, black dots show the average $\pm \sigma$.

The wide ranging and inconsistent response from devices to a water (“blank”) solution, as shown in Figure 6.14, is perhaps the biggest obstacle to sensing glucose concentrations less than about 200 μM . In Figure 6.20, the change in current over the 800 seconds for the 200 μM analyte in that data set was approximately 1 μA and in the DI water (0 μM glucose) was between 0.5 μA and 1 μA , however Figure 6.14 shows that the response to DI water analytes can vary significantly and that changes in the order of 1 μA are observed, indicated that 10 μL of 200 μM solution may be approaching the minimum measurable concentration using this system. In addition, the inherent device-to-device variation (as observed for all types of OTFTs presented in this thesis) means that the same analyte does not always give the same response.

Despite the present limitations, comparing data collected within sets of devices made and tested under the same conditions (that is, on the same day) tend to show a monotonic relationship between glucose concentration and increases in I_D , particularly for glucose concentration towards the higher end of those examined here (as in Figure 6.20). Therefore, improvements in device consistency and perhaps refinements in device architecture to make the channel area more susceptible to increases in protons are perhaps the biggest challenges to achieving a reliable OTFT-based glucose sensor.

6.10 PVPy Dielectric Layers in Nafion:GOX Gate Devices

As mentioned earlier, some disadvantages of the P3HT/PVP/Nafion:GOX devices are apparent on observation of their output characteristic. These include a low current modulation ratio and a poorly defined saturation region when compared with the “standard” PVP-based devices introduced in Chapter 3. Here, the results of a short study looking at the electrical characteristics of P3HT/PVPy/Nafion:GOX and their response to glucose analytes are presented.

Figure 6.28 and Figure 6.29 show the output and transfer characteristics respectively for a device with a PVPy dielectric and a Nafion:GOX gate electrode. This behaviour is very similar to the PEDOT:PSS-gated PVPy dielectric device in that it shows lower I_{ON} and I_{OFF} than a standard device and $|V_{TH}|$ is increased. Compared with the PVP/Nafion:GOX devices, there are well-defined linear and saturation regions. Figure 6.30 shows that once again the I_G levels are decreased significantly when PVPy is employed, similarly to the change observed when replacing PVP with PVPy in devices with a PEDOT:PSS gate. Despite the relatively favourable performance of OTFTs made with a PVPy dielectric and a Nafion:GOX gate, the fact that PVPy restricts the movement of H^+ in the devices was of concern for use in glucose detection given that the sensing mechanism relies on the liberation and subsequent movement

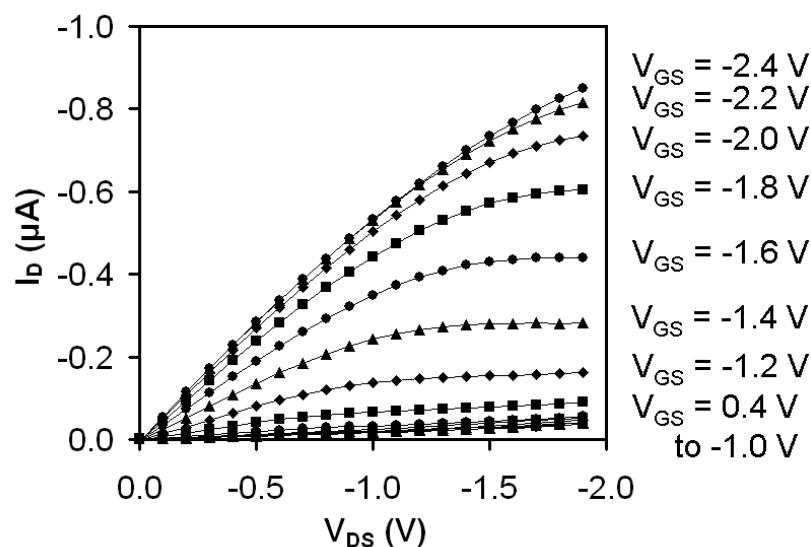


FIGURE 6.28: Output characteristic for an OTFT with a PVPy dielectric layer and a Nafion:GOX gate.

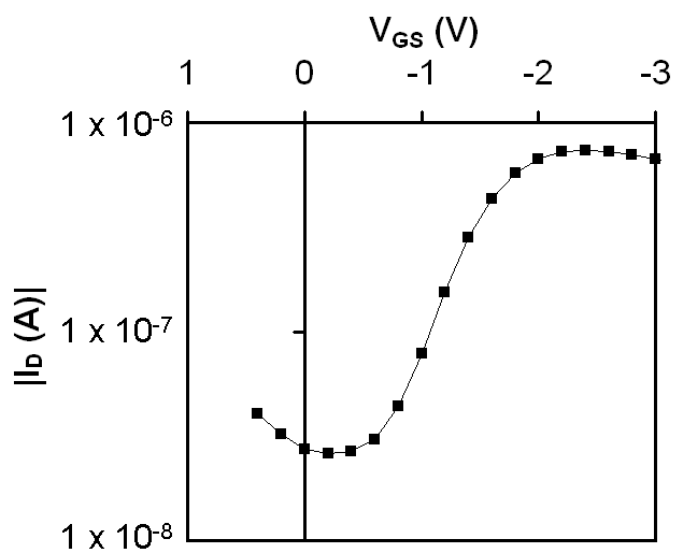


FIGURE 6.29: Transfer curve of an OTFT with a PVPy dielectric layer and a Nafion:GOX gate obtained from the output characteristic at $V_{DS} = -1.5$ V.

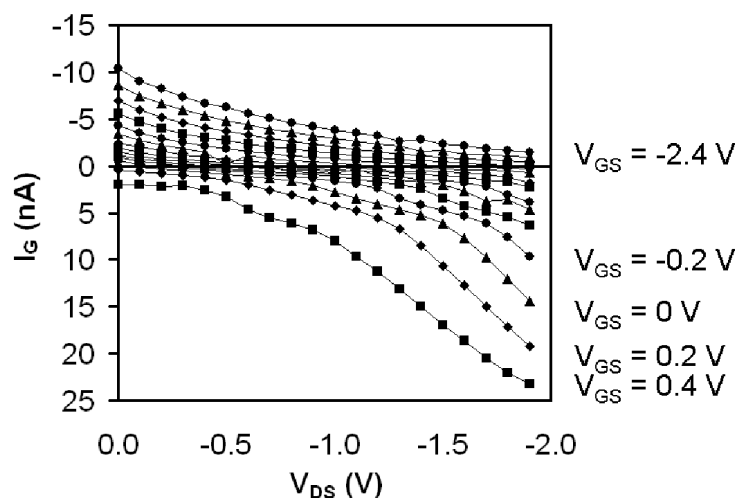


FIGURE 6.30: Leakage currents of an OTFT with a PVPy dielectric layer and a Nafion:GOX gate.

within the devices of H^+ .

Figure 6.31 shows the current response versus time for two glucose solutions ($8 \mu\text{M}$ and 30 mM) dropped onto P3HT/PVPy/Nafion:GOX devices. The data presented so far in this chapter shows that there is a marked difference in the response to analytes of these two concentrations when using PVP-based devices. The analyte volumes were $10 \mu\text{L}$ and the GOX concentration was 20 mg/mL in the Nafion solution as was the case in the data presented for the device with a PVP dielectric. The initial current level (prior to analyte addition) was lower in the PVPy devices than the PVP devices (0.01 to $0.1 \mu\text{L}$ down from about $10 \mu\text{L}$), which was promising in terms of reducing any background signal impacting on the signal-to-noise ratio. However, almost no difference is observed in the responses presented in Figure 6.31. However, the lack of differentiation between these two concentrations (at opposite ends of the scale of concentrations for the data presented for PVP-based devices) seems to confirm the hypothesis that PVPy restricts the impact of changes in proton count on I_D .

6.11 Conclusions and Future Work

In this chapter, OTFT-based enzymatic glucose sensing has been investigated. A clear trend between the changes in I_D after analyte solutions are dropped onto the device and glucose concentration is observed for glucose concentrations between 0.2 mM and 30 mM . At lower glucose concentrations the relationship is difficult to determine due to variations in device characteristics, however there is an overall trend of the results

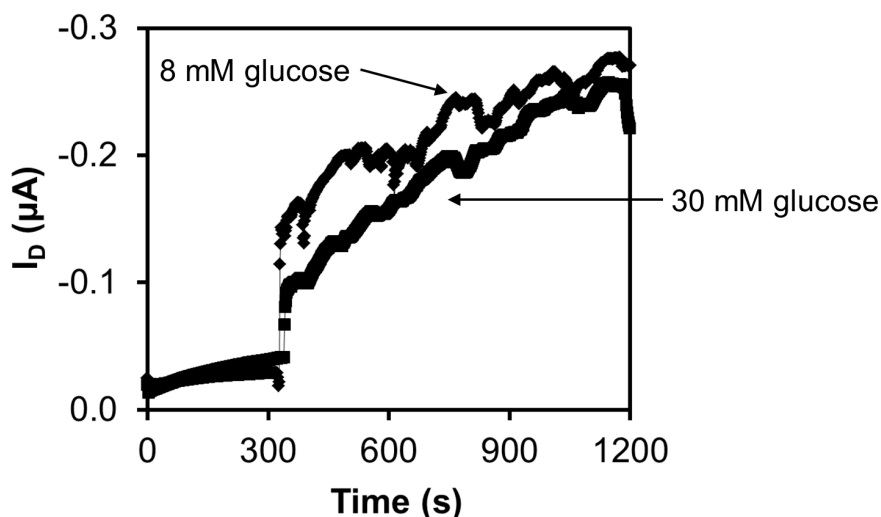


FIGURE 6.31: I_D versus time for a strong (30 mM) and weak (8 μM) glucose solution dropped on the devices at $t = 300$ s.

which carries into the region lower than 0.2 mM albeit with increased error. Furthermore, work conducted with H_2O_2 analytes indicates that there is potential for sensing lower concentrations using this technique. Since measurements conducted on a particular day tend to yield current increases in monotonic relation to glucose concentrations between 0.2 mM and 30 mM, improvements in device consistency could be a way to realise reliable glucose detection. Coupling of the enzyme response to the channel area could also likely be optimized through changes to the device architecture. Since the saliva-glucose level has a correlation to the blood-glucose level, improvement in the sensitivity for lower glucose concentrations will allow for the development of an unobtrusive blood-glucose measurement device with all the advantages of an OTFT.

The work presented here is intended to be a “proof of concept” for this type of sensor. The results shown above provide enough encouragement for further development of such devices. Furthermore, it is anticipated that this type of sensor could be a model platform for employing other enzyme-based reactions in a simple OTFT-based sensor.

7

Conclusion

Over the course of this thesis, the electrical characteristics of certain types of organic thin-film transistors designed for sensing applications have been presented and discussed. By probing these devices in different ways, much has been learned about the mechanisms behind their operation as well as how they compare with other types of transistors. All of these devices have the capability of being fabricated in air using simple techniques.

In Chapter 3, organic thin film transistors which exhibit operation at low voltages were introduced. The devices' low-voltage operation can be attributed to the hygroscopic nature of their PVP dielectric layers. The work presented in this section aimed to build on the work already published by Österbacka's group on similar devices. The properties of the devices were thoroughly examined and inferences were made about their operating mechanisms. It was shown that the most likely mechanism for current modulation in PVP-based OTFTs involves doping and de-doping of the P3HT layer by mobile ions within the device.

Chapter 4 detailed the introduction of a new dielectric material (PVPy) in an attempt to reduce the off current of the devices, and, in turn, increase their current modulation ratio. Transistors with a high current modulation ratio can switch between a wider range of currents therefore being more useful as switches or amplifiers. I_{OFF} was successfully reduced; however, an associated decrease in I_{ON} resulted in no substantial increase in current modulation ratio. Nonetheless, this result exhibited the potential advantages of changing the materials in a device in order to tune its properties.

In Chapter 5, devices with PVPy dielectrics were again presented; this time, though, the PVPy was doped with two different types of salts. The aim of this doping was to enhance current modulation by providing additional mobile ions in the device. These

devices showed an improvement of many orders of magnitude in the current modulation ratio when compared with their undoped counterparts, greatly increasing the potential practicality of this type of OTFT. The effect on device performance of different ionic species was discussed and helped to confirm the moisture-rich environment existing in the dielectric layer of these OTFTs due to ions moving in accordance with a hydration sphere model.

The potential for OTFTs to be used as a platform for enzyme-based biosensors was outlined in Chapter 6. The high level of biocompatibility of the organic materials used in these transistors allows for the inclusion of enzymes within the devices which would not be possible with the materials and fabrication steps used in the production of conventional transistors. As an example, glucose oxidase was incorporated into the gate of an OTFT and its enzymatic activity was confirmed after undergoing fabrication, thus enabling the detection of glucose with such a device.

7.1 Future Work

The work presented here forms the basis for several strands of study in the future. One area for further research would be to investigate the effect of using a wider variety of salts (and hence ions) in the dielectric layers of the doped-PVPy devices. In the work presented in Chapter 5, only LiClO_4 and NaClO_4 were employed as dopant salts. This investigation was enough to demonstrate that the current modulation ratio can be greatly enhanced compared with undoped devices, and the comparison between sodium and lithium cations showed how the use of ions of varying sizes and hydration spheres can affect the device properties. However, experimenting with a wider variety of ions in the dielectric layer of the PVPy-based devices could lead to the determination of an optimal combination of cation and anion to maximise the OTFT performance, as well as reveal more about the transport properties of PVPy itself.

Secondly, although the doped-PVPy devices show remarkable performance in terms of operating voltage, current modulation ratio and sub-threshold swing, their response is relatively slow. If their response can be improved so that they can be switched on and off at speeds of, for instance, greater than 1 Hz, the range of their potential applications would be greatly increased. Recently, there has been evidence of organic transistors based on electrochemical mechanisms operating at significantly faster speeds [122, 123], so hopefully increases in operational bandwidth will be achievable in the future.

Another possible field for further work is the optimisation of the response for glucose when glucose oxidase is embedded into the device. Obtaining high sensitivity in the glucose-in-saliva region should be the ultimate goal of this type of sensor. This could come via one or more of several approaches: optimising the architecture of the devices to more effectively couple the analyte with the enzyme, improving the consistency of characteristics from device-to-device through improvements in fabrication

methods and developing or a more effective way of extracting the enzymatic response from the current characteristics. In addition, the introduction of other enzymes into the devices should be a relatively straightforward way to expand the number of potential applications by targeting a variety of analytes.

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