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Investigation into memory effect in organic semiconductor devices

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Investigation into Memory Effect in Organic Semiconductor Devices

Stephen Anak William

Ph. D. Thesis, 2006 University of Wales, Bangor to Seow Tien Yeo -whose words and tears gave me courage and strength.

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Abstract

The works reported here were divided into two parts. In the first part of an investigation, the memory effect in polymer memory diodes based on poly (4dicyanomethylene-4H-cyclopenta [1,2-b;3,4-b'] dithiophene (PCDM) is described. The second part describes a study of a flash memory device using regioregular poly (3-hexylthiophene) (P3HT) as an organic semiconductor and polysilsesquioxane (PSQ) as an insulator. In the polymer flash memory device, a thin gold layer (20 nm) embedded in the PSQ insulator was used as a charge storage element. In both parts, the memory effect was studied by means of DC current-voltage (I-V) measurements and admittance spectroscopy. In the first part, the disappearance of the memory effect in the later PCDM films produced successively from the same monomer solution have been further studied by the FTIR and UV/Vis spectroscopy. In the second part, the precursor devices such as P3HT Schottky diode, metal-insulatormetal (MIM) and metal-insulator-semiconductor-metal (MISM) which ultimately led to the floating gate memory device were also fabricated and investigated.

The changes in the electrical characteristic of the PCDM films were consistent with the spectroscopic data. It is suggested that free BF₄ anions create a space charge region at the interfaces leading to the memory effect shown in the first two PCDM films. Quaternary ammonium counter-cations become trapped in the later PCDM films as demonstrated by the FTIR spectrum and in turn bind the BF₄ anions. As a result, the memory effect in the later films disappeared. In MIM device, PSQ film shows a very good insulating property in voltage and temperature range of -40 V to 40 V and 25°C to 130°C respectively. By comparing the results of the precursor devices with the flash memory device, it was shown that the embedded floating gate in the insulator created a site for charge trapping. Hysteresis was observed in both the I-V and C-V plots of the flash memory device with a threshold voltage shift of \sim 7.5 V in the C-V plot when the device was subjected to the voltage sweep range \pm 20 V. It is also suggested that the PSQ insulator only allows electron transport.

1.1 Background of Memory Device

A memory device is defined as any device that can store or preserve data or information for later retrieval. Memory itself can be split into two main categories: magnetic and semiconductor. Magnetic memories can be in the form of magnetic disk, tape, drum or core. In fact, the earliest computer memory was made up from magnetic cores which consisted of small magnetic rings to store the data in the polarity of the magnetic field they contain. Semiconductor memories meanwhile are further classified into two types: volatile and non-volatile. Volatile memory loses any data as soon as the system is turned off and it requires constant power to remain viable. On the other hand, nonvolatile memory does not lose its data when the power is turned off for a certain period of time. Barr [1] has classified semiconductor memories into three main categories as shown in figure 1.1.



Figure 1.1 Common memory types in computer system (adapted from [1]).

It is clearly illustrated in figure 1.1 that semiconductor memories can be divided into RAM (random access memory), ROM (read only memory) and hybrid (a

combination of RAM and ROM). Generally, RAM is unable to retain the data whenever the power is switched off, which fulfilled the criteria of being volatile memory. In addition the difference between static-RAM (SRAM) and dynamic-RAM (DRAM) is the lifetime of the data they store. SRAM is able to retain the data for as long as the power is turned on, whereas DRAM only retain the data for a very short period of time, even when the power is switched on the data might be loss. On the other hand, ROM is a non-volatile memory, where once written, the data will be stored even after the power is turned off. Data stored in both programmable-PROM (PROM) and masked ROM are inerasable and the only difference between these two types of memories is that PROM comes in as an un-programmed state whereas masked ROM is a preprogrammed memory device. Meanwhile, erasable-PROM (EPROM) is the type of PROM that can be erased and reprogrammed. The data in EPROM can be erased by exposing the device to a strong ultraviolet light source.

Finally, as memory technology has advanced in the last decade, the most important types of memory device are ones which combine the features from both RAM and ROM which can be collectively be referred to as hybrid memory devices. In hybrid memories, the data can be read and written which make it more like RAM but at the same time their contents can be maintained even after the power is turned off, which resembles the ROM features. The first hybrid memory device was a non-volatile-RAM (NVRAM) which originated from SRAM and usually holds persistent data. Another two hybrid devices are electrically-EPROM (EEPROM) and flash, which originally came from the ROM family and both are typically used to store code. We will not go further in detail explaining the types of memory device which is outside the boundary of this study. In the following section, we will limit our discussion to

the methods of fabricating the memory devices, from inorganic memory to organic memory devices.

Semiconductor memories can be achieved by two different technologies, i.e. Metal-Oxide Semiconductor (MOS) technology or bipolar technology. Bipolar transistors are semiconductor devices whose operation relies on both majority and minority charge carriers. Basically, all p-n junction based memory devices can be considered as bipolar devices. In around 1968, almost all integrated circuit (IC) were made up from bipolar technology and MOS technology was still in the infant stage. With the advancement of silicon gate technology, however, MOS technology has replaced bipolar technology as a main pathway in fabricating a more complex IC. However, in this thesis, we focus only on the modified MOS with an addition of a charge trapping layer in the gate insulator and a simple memory diode which resembles a tunnel diode memory device.

In the last few decades, silicon technology has progressed tremendously which has enabled the development of very high performance IC. This high performance IC was realized by the high speed and integration density of devices fabricated in monocrystalline silicon. Nowadays, one can find very high performance IC in every high-end electronic product such as personal computers, telecommunication systems, robotics technology and other portable devices. Given this situation, one could conclude that there is no room for any other material in electronic devices and every single electronic device should be made from monocrystalline silicon. However, with such a performance, monocrystalline silicon device faces its own limitation, which is the high cost of device fabrication. Therefore, this leaves a gap for other

materials to fulfil in low-end products which require large-area coverage, good mechanical properties and the most importantly low manufacturing cost.

1.2 Alternative Materials for Memory device

There are a few cheaper materials that could possibly be alternatives to monocrystalline silicon in fabricating memory devices such as ferroelectric materials, nanocrytals and organic semiconductors.

1.2.1 Ferroelectric Material Memory Device

A ferroelectric material is a material that has a permanent electric dipole moment which might be reoriented by the application of an electric field. Much attention has been paid to the possibilities of utilising ferroelectric materials in memory devices [2 -23]. Xiong et al [2] illustrated switching in the ferroelectric using the diagram shown in figure 1.2. The switching is generally considered to consist of three steps. Firstly, the inhomogeneous nucleation of new domain starts at the electrode surface or at a grain boundary. This new domain has to reach a critical size for further growth or otherwise it will shrink and disappear.



Figure 1.2 *Switching kinetics of ferroelectric thin film (a) inhomogeneous nucleation,* (b) forward growth regime, and (d) lateral growth regime (from Xiong et al [2]).

Shown in figure 1.2 (a) are new domain walls that have already reached a critical size. The second domain wall then move from anode to cathode or vice-versa in a needle-like one-dimensional shape and form stable cores (figure 1.2 (b)). Finally, the domains spread out laterally from these stable cores and fill the entire volume of the ferroelectric film (figure 1.2 (c)). Based on this switching principle, Xiong et al [2] demonstrated that their ferroelectric FET memory device has an 'ON' and 'OFF' ratio of six orders of magnitude with a threshold voltage shift of 3V and their writing voltage was ± 4 V.

1.2.2 Nano-crystal Memory Device

The term nano-crystal in this thesis represents any metallic island structure embedded in the insulator of the metal-insulator-semiconductor (MIS) memory device and includes nano-particles, nano-clusters, quantum dots, etc. Basically, nano-crystal memories utilize the Coulomb blockade effect in small geometries and distributed charge storage. Coulomb blockade is based on the charging energy of a small capacitor and allows the transport of single electrons. If a charge Q is brought onto a capacitor with capacitance C_T , the stored electrostatic energy E_c of the capacitor is given by,

$$E_C = \frac{Q^2}{2C_T} \,. \tag{1.1}$$

If this charge is a single electron, the charging energy is normally very small compared to the thermal energy. This energy will only be significant in extremely small capacitors. One implementation of such a small capacitor is a small island connected to two electron reservoirs by tunnel barriers. Electrons can only be transferred from one reservoir (source) to the other (drain) by tunneling. If electrons are to tunnel onto the island, the capacitor must be charged. Therefore a threshold bias voltage (V_T) is needed for electron transport.

Below this voltage, electron transport is suppressed and no current is observed, as shown in the current-voltage characteristic in figure 1.3. Only when a larger voltage is applied can electrons tunnel onto the island and further to the other reservoir. In this case only single electron transport occurs. The suppression of the current at low bias is called "Coulomb blockade" and the region below the threshold voltage is called the "Coulomb blockade region" [24-26]. The primary motivation in the use of nano-crystal memories is the potential to scale the tunnel oxide thickness to a small dimension resulting in lower program and erase voltages during operation.



Figure 1.3 Current-Voltage characteristics of the device under Coulomb blockade.

1.2.3 Organic Semiconductor Memory Device

Ferroelectric and nano-crystal materials as discussed above might provide an alternative to silicon in memory device manufacturing especially for a low-end product. However, the uniqueness of organic materials give them advantages over other materials in terms of low fabrication cost, high mechanical flexibility and versatility of the chemical structure. As a result, during the past 20 years, many organic devices have attracted considerable interest especially in the area of transistors [27-38], light-emitting diodes [39-52] and photovoltaic cells [53-56]. On the other hand, not until the last five years did electronic memory using organic

materials attract much interest among the researchers, although the first discovery of the memory effect in organic devices was reported by Carchano and co-workers in 1971 [57]. After that the field of organic memory devices did start to flourish but at a very slow pace. Some of the organic materials that have shown some promise in memory devices are polymethylmethacrylate (PMMA), polystyrene, polyetylmethacrylate (PEMA) [58, 59], tetracyanoquinodimethene (TCNQ)-based polymer [60-62], melamine cyanurate (MC) [63], 2-amino-4,5-imidazoledicarbonitrile (AIDCN) [64, 65] and thiophene-based polymer [66-69].

1.3 Current Trend in Organic Memory Device

At the beginning of the study of the organic memory devices, many researchers paid attention to the possibilities of fabricating a simple device such as memory diode or memory transistor. However, as their counterpart in the inorganic memory device have shown, embedded technology proved to be a successful means to fabricate a perfect memory device. So unsurprisingly, the early versions of organic memory devices were far from practical in memory application, especially in non-volatile memory application. One of the main reasons for this failure might be due to the fact that there are no coherent trapping sites available in those organic materials that can act as a storage element.

Therefore, integrating the idea of using a floating gate memory device which was first discovered by Kahng and Sze [70] in 1967 and floating gate-avalanche MOS (FAMOS) transistors [71], some of the researchers have incorporated metal nano-

particles in the multilayer organic semiconductor films [64, 65, 72], in the polymer insulator [73, 74] or in the silicon-organic hybrid [75]. In all these devices, the most important parameter in determining the performance of the memory device is the size of the nano-particles. More importantly, Ma et al [65] revealed that the size of the metal-nanocluster in their device is absolutely critical, whereby the memory effect will be absent in the device with different metal-nanocluster sizes. The difficulty of controlling the nano-particle size might jeopardise the realisation of the low-end organic memory device. So the solution to this problem might be the use of a continuous floating gate embedded in the insulator of the organic memory device.

1.4 The Outline of the Thesis

This study is divided into two main parts. The first part is a follow-up study of the switching and memory effects in poly (4-dicyanomethylene-4H-cyclopenta [2,1-3,4-b']dithiophene) (PCDM) diodes which was discovered by Mills and co-workers [68, 69]. The aim of this part was to explore the possibility of using PCDM in fabricating a new organic memory device. The second part concentrated on the fabrication of a new organic flash memory device which resembled an inorganic floating-gate memory device.

In Chapters 2 and 3, the theoretical frameworks which might relevant to the main thesis were discussed. Chapter 2 is especially dedicated to a discussion of the polymer with extra attention paid to the origin of semiconduction in polymers. In addition, the theory underlying several conduction mechanisms was also

incorporated in chapter 2 as a basis for interpreting charge transport in the final devices. Chapter 3, meanwhile, is focused on the theory of the Schottky diode and metal-insulator-semiconductor (MIS) capacitor together with their respective equivalent circuits. In Chapter 3, we also describe the mechanisms of the memory effects that are relevant to the interpretation of the results obtained from our devices.

In Chapter 4, the reader can find information about the materials and the experimental methods employed throughout this study. The main materials used in this study are well-known materials such as PCDM, poly(3-hexylthiophene), and polysilsesquioxane (PSQ). Therefore in the material section only a brief description of these materials is given.

Chapter 5 presents the result of the PCDM memory device. In this chapter the spectroscopy data as well as electrical data were used to clarify the reason behind the sensitivity of the effect on the growth conditions.

Chapter 6 describes a systematic study of different device structures which ultimately led to the flash memory device. The chapter starts with the results of a typical ITO/P3HT/Al Schottky diode, followed by an ITO/PSQ/Au MIM device, an ITO/PSQ/P3HT/Al MISM device and finally an ITO/PSQ/Au/PSQ/P3HT/Al flash memory device. The results of these four devices are compared to draw conclusions on the possibilities of fabricating a flash memory device from our final device. Finally Chapter 7 highlights the overall conclusion from this study and possible future work is also recommended.

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2.1 Introduction

Popularly known as 'Plastics', polymers are large molecules constructed from smaller structural units (monomers) covalently bonded together in one of a number of different patterns. The special properties of polymers allow a variety of convenient processing methods, such as injection moulding, spin coating, spray painting, electrodepositing and self-assembling. This is in striking contrast to the processing of metals and even more so, inorganic semiconductors such as silicon. Hence, polymers can be found in almost all products in our present day society: clothes, furniture, home appliances, cars, airplanes, electronics, etc. There exist naturally occurring polymers such as proteins, carbohydrates and rubber, but most polymers in use today are synthesized, and hence are called synthetic polymers.

Since the Nobel Prize winning discovery and development of conducting polymers by A. J. Heeger, A. MacDiarmid and H. Shirakawa in 1976 [1], the field of conducting and/or semiconducting polymer research has grown at a dramatic pace. The key discovery by Heeger and co-workers was that the conductivity of polyacetylene (PA) (see figure 2.1) increased from about 10^{-9} S/cm to about 40 S/cm when doped with iodine (I₂).



Figure 2.1 The chemical structure of poly-acetylene [1].

A conductivity of less than 10^{-6} Scm⁻¹ is considered as insulating, whereas conductivities ranging from 10^{-6} Scm⁻¹ to 10^{2} Scm⁻¹ fall in the semiconductor category while metallic conductivity is greater than 10^{2} Scm⁻¹. As clearly illustrated in figure 2.2, conjugated polymers have conductivities spanning the range from insulators to that of the metals. Therefore, one can choose an appropriate conjugated polymer to fabricate a specific device.



Figure 2.2 The conductivity of polymers compared to inorganic materials [2].

In polymers, there are two major types of bond (i.e. π and σ) connecting atoms that form the polymer. Hybrid atomic orbitals (S and P) form σ -bonds while overlapping P orbitals form π -bonds. Two orbitals overlapping end-to-end form the σ -bond skeleton, lying directly between the nuclei; such bonds are localised. Figure 2.3 shows three basic types of atomic orbitals in the polymers structure, i.e. SP³, SP², and SP. The SP³ orbital is found in saturated polymers such as polyethylene. The SP² is normally associated with an unsaturated polymer where a double bond is present between two carbon backbone atoms while the SP orbital is found in polymers which are highly unsaturated and have triple bonds between two carbon atoms.



Figure 2.3 Atomic orbitals in polymers; grey represent the main orbitals, circular bubble represent the first P-orbital, and small-white dot represent second P-orbital.

On the other hand, two P orbitals directed perpendicular to the σ -bond can overlap sideways, and may easily encounter other adjacent P orbitals thus extending the overlap further. Such a situation could create a more extended π orbital in which the electrons in the orbital are no longer confined between two atoms but rather are delocalised over a greater number of nuclei. The formation of these two bonds is illustrated in figure 2.4.



Figure 2.4 *The formation of* σ *and* π *bonds in polyacetylene.*

The delocalisation of π electrons is of central importance to the chemical and physical properties of unsaturated molecules. The unsaturated molecules involved are those which have formal structures exhibiting alternating double bonds (or two unshared electron pairs which can be hybridised into a P orbital) and therefore capable of further π overlap with each other. Such unsaturated molecules are said to be conjugated and to have conjugated double bonds. Saturated polymers (with no double bond) are normally non-conducting, whereas unsaturated polymers with conjugated double bonds are normally conducting or semiconducting.

However the degree of their conductivity depends on the band-gap between the conduction band (CB) and valence band (VB) of the particular polymer. Therefore in

classifying polymers into conducting and non-conducting materials, the most appropriate way is to divide them on the basis of their band-gap, as in Table 2.1.

 Table 2.1: Classification of polymers in terms of band gap.

Materials	Band-Gap (eV)
Non-conducting polymer (insulator)	> 6
Semiconducting polymer	≤2
Conducting	CV & VB overlap

Non-conducting polymers normally have a band gap > 6 eV, which is too large for the electron to surmount even under extreme condition, such as high temperature and high light energy. However, in semiconducting polymers with a band gap ~ 2 eV, under certain circumstances such as at higher temperature, electrons can be thermally excited from the valence band to the conduction band. In conducting polymers on the other hand, the conduction and valence bands overlap allowing easy energy transitions.

In order to understand further the classification of polymers into conducting and insulating polymers, the energy band diagram in figure 2.5 is helpful. Figure 2.5 shows the difference between the discreet energy levels in a single atom (a) and energy bands in complex molecules (b). Every single atom in a polymer has discrete energy levels. When many atoms come together to form a complex molecule or polymer, their energy levels are slightly modified and form an energy band. From figure 2.5, π and π^* orbitals split to form the valence and conduction bands respectively with an energy gap Eg, arising from the Peierls instability.



Figure 2.5 Energy band diagram of polymers (a) discreet energy levels in single atom and (b) energy bands in complex molecules.

In the absence of this phenomenon, the potential of the electrons along the carbon backbone is constant since every carbon-carbon bond has the same length in which case the conduction and valence band overlap forming a metallic-like material as opposed to a semiconductor. As a result the energy band will be half-filled (see figure 2.6 (i)). In reality, however, the coupling of phonons and electrons render this one-dimensional system unstable resulting in an alternation of the double-bonds between two consecutives carbon atoms (see figure 2.6 (ii)). This dimerisation of the carbon atoms involved in the conjugated backbone of the polymer chain leads to the opening of a gap between the π and π^* orbitals with electrons filling the lower energy π -band.

The formation of the energy bands of poly(4-dicyanomethylene-4H-cyclopenta[2,1b:3,4-b'] dithiophene (PCDM) has been illustrated by Salzner [3] as shown in figure 2.7. The discrete energy levels of the monomer are seen to split upon forming the dimer and to split even further in the trimer. In the polymer, the discrete levels form a quasi-continuum of states which split into a conduction and valence band separated



by a forbidden energy gap. As outlined above, the band gap arises from the Peierls instability.

Figure 2.6 The formation of the alternate double bonds in conjugated polymer (i) The potential of the electrons along the chain is constant and (ii) the effect of Peierls instability in the conjugated polymer.

The past decade has witnessed tremendous advances in the development of organic conductive molecular and polymeric materials and the field continues to be of great scientific and commercial interest. Of particular importance has been the discovery
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that the electrical conductivity of π -conjugated materials could be changed from semiconductive to metallic to a superconductive regime when doped [1].



Figure 2.7: Energy levels and development of bands for PCDM. (a) Monomer CDM, (b) dimer, (c) trimer and (d) is the energy band for PCDM with an energy gap of 1.72 eV (adapted from [3]).

One may argue that polymers will never be able to compete with inorganic semiconductors in high speed and complicated applications such as microprocessors. To an extent such arguments may be countered by considering the photosynthesis process; here a polymer (chlorophyll) utilises light from the sun as an energy source to make food (carbohydrate). As we know, the photosynthesis process is very complicated, but still a polymer can perform this task.

To date, some progress has been made in producing electronic devices from polymers. The most studied device is the light emitting diode (LED) following the initial discovery by Burroughes et al [4] at the University of Cambridge. The first LED fabricated was a simple single layer device consisting of a thin poly(*p*phenylene vinylene) (PPV) film spin-coated onto an indium tin oxide (ITO) covered

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glass substrate and onto which an aluminium counter electrode was deposited. The device is depicted in figure 2.8.



Figure 2.8 Schematic diagram of the first single layer polymer light emitting diode.

Nowadays, this device has found its own niche in the consumer market especially as a backlight in mobile phones. There are a few more devices that may make their way into commercial products such as polymer solar cells, solid state polymer lasers, RFID tags and electronic inks.

In almost any electronic application, transistors are needed and some researchers have tried to fabricate all polymer transistors. Unfortunately, until recently conducting polymers as well as their shorter oligomers i.e. homologues had a low mobility, typically $\sim 10^{-2}$ cm²/Vs or less in non-ordered films. However, some molecular materials such as pentacene have mobility comparable to amorphous silicon. The mobility of purely organic semiconductors seems to have reached its maximum value and little has changed since the late 90s. This has led to the emergence of the hybridization of organic and inorganic semiconductors which have achieved mobility close to that of poly-silicon (see figure 2.9).



Figure 2.9 The evolution of the mobility of the organic semiconductor [5].

Hybridization of the organic-inorganic materials has enabled the integration of desirable characteristics of the organic and inorganic material within a single molecular-scale composite. Therefore the organic-inorganic hybrid has a wide range of desirable physical properties such as high fluorescence efficiency, large polarizability, ease of processing, good flexibility and versatility of the structure which are the physical characteristics of the organic materials. In addition, this new class of material also has the physical properties of inorganic materials such as a wide range of electronic properties, magnetic and dielectric transitions, good mechanical hardness, and good thermal stability. As a result, the mobility of organic-inorganic hybrids (e.g. phenethylamine-tin iodide) has improved substantially and is comparable to the mobility in amorphous silicon (see table 2.2).

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Table 2.	2 Comparison	of the	mobility	of	organic-inorganic	hybrid	materials	with
other mai	erials [5].							

Semiconductor	Representative chemical structure	$Mobility (cm^2V^1s^{-1})$
Silicon	Silicon crystal	300 - 900
	Polysilicon	50 - 100
	Amorphous silicon	~1
Pentacene		~1
α,ω-dihexyl- sexithiophene	α, ω -dihexyl- sexithiophene $\gamma \gamma \gamma$	
α,ω- dihexylanthra- dithiophene	statistics server	10-1
Regioregular poly (3- hexylthiophene)		10 ⁻¹
Organic- Phenethylamine-tin-iodide inorganic hybrid		~1

Furthermore, a considerable effort has been required to improve the efficiency of carrier injection into the structures and much remains to be done especially in the understanding of interfaces between polymer and metal. This is of primary importance in fabricating devices of the highest efficiencies. Rectifying Schottky barriers formed between semiconductors and metals have long provided information on the electrical properties of the polymer.

2.2 Type of Polymer Semiconductor

Tremendous efforts have been made by organic chemists from all over the world to optimise the properties of polymer semiconductors to meet the need for cheap electronic products such as mobile phone displays, identification system such as radio frequency identification tags (RFIDs), badges or smart cards or even wearable computer. This effort has led to the discovery of organic materials that can match the mobility of amorphous silicon. There are many types of conjugated polymer that might behave as a semiconductor materials as shown in figure 2.10.

In the first generation of conducting polymers, the electrical conductivities were limited. However, due to the success of the doping process, the electrical conductivity of certain polymers can be increased close to that of a metal such as copper. Charge injection into the polymer (doping process) can be achieved in a number of ways as summarized by Heeger [6] in figure 2.11.

The first doping technique to emerge was the ability to dope conjugated polymers by charge transfer redox chemistry. This technique is known as chemical doping and can be divided into two types [1, 7];

(a) oxidation – p-type doping

$$(\pi - polymer)_n + \frac{3}{2}ny(I_2) \rightarrow [(\pi - polymer)^{+y}(I_3^-)_y]_n$$
, and

(b) reduction – n-type doping

$$(\pi - polymer)_n + n[Na^+(Naphthalide)]_y \rightarrow [(Na^+)_y(\pi - polymer)^{-y}]_n + n(Naphth)^{-y}$$



Figure 2.10 A few types of conjugated polymer with their molecular structure [6].

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Figure 2.11 General doping mechanisms (adapted from Heeger, [6])

Chemical doping can be found in several situations such as transparent electrodes, antistatic EMI shielding, and conducting fibres. While, chemical doping can be used relatively easily to achieve high conductivity by heavy doping, any attempt to achieve an intermediate doping often results in inhomogeneous doping. Therefore, electrochemical doping was developed to overcome this problem [8]. In electrochemical doping, the voltage between the conducting polymer and the counter-electrode controls the doping density in the polymer. The doping process stops when electrochemical equilibrium is reached. So, by applying a certain voltage, one can control the doping density at any stage. The example of electrochemical doping illustrated in figure 2.12 is for p-type doping and can be summarised as [6];

$$(\pi - polymer)_n + n[Li^+(BF_4^-)]_{sol'n} \rightarrow [(\pi - polymer)^{+y}(BF_4^-)_y]_n + nLi_{(electrode)}.$$

The third doping technique is interfacial doping which involves the injection of charges at the metal-semiconductor polymer interface. When electrons are added to the π^* -band, the polymer is reduced. On the other hand, when electrons are removed

from the π -band, the polymer is oxidised. This doping technique differs from chemical and electrochemical doping since the counter-ions are absent, and occurs in organic FET and LED devices. Finally, photochemical doping can also occur where light is used to dope the polymer following the reaction;

 $(\pi - polymer)_n + hv \rightarrow [(\pi - polymer)^{+y} + (\pi - polymer)^{-y}]_n$.

The polymer is locally oxidised and reduced by photo-absorption and charge separation [6]. Basically, this doping technique is useful to dope the polymer for photovoltaic devices.



Figure 2.12 *Schematic diagram of the electrochemical cell. The cathode is the working electrode coated with polymer film while the anode is the counter-electrode.*

Normally a pristine polymer has a broad band gap, hence it is not a good semiconductor material. Unlike conventional silicon material, a polymer can be doped to produce a very narrow band gap polymer. In order to increase the conductivity of the polymer we have to dope it with suitable dopant e.g. tetratbutylammonium tetrafluoroborate.

In conducting polymers with a non-degenerate ground state (such as polythiophene) the charge introduced upon doping can be stored in the form of polarons and bipolarons. The formation of polarons and/or bipolarons induces a change in the phase of the double bonds and the creation of a domain with a quinoid sequence of double bonds. The doubly charged bipolaron is spinless whereas the polaron possesses one charge and one spin. The creation of polarons and bipolarons cause a significant change in the electronic spectrum of the polymer which involves bleaching of the π - π * transition peak with the simultaneous growth of bands in the lower energy part of the spectrum associated with polarons and/or bipolarons [9].

While there are many conjugated polymers that show semiconductive properties, in the following section we will concentrate the discussion on the two conjugated polymer semiconductors that were used in this study, namely (1) poly(4dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b'] dithiophene (PCDM), and (2) poly(3-hexylthiophene) (P3HT). Both of these conjugated polymers are thiophenebased polymers, which consist of a thiophene ring backbone but different side chain groups.

2.2.1 PCDM

Ferraris and Lambert [10] produced PCDM film by electropolymerisation of the CDM monomer. CDM monomer was synthesised by using a multi-step synthesis process previously outlined by Jordans and co-workers [11]. Although, there were many initial steps involved in the production of the CDM monomer, the final step is summarised in figure 2.13. As indicated in figure 2.13, malonitrile $(CH_2(CN)_2)$ was added to the cyclopenta [2,1-b:3,4-b'] dithiophene-7-one (CDT) and both were dissolved in ethanol and a few drops of piperidine were added. More detail about the preparation of the CDM monomer can be found in Mills [12].



Figure 2.13 Conversion of CDT to CDM.

PCDM being a non-degenerate polymer has a relatively large energy band gap which has been quoted as 1.72 eV [3] or 1.38 eV [12]. Therefore we have to dope it to a certain extent to enhance the electron and hole transport and hence the overall performance of the device that may be produced from this material. When we dope the PCDM film, polaron as well as bipolaron levels (states) will be formed close to the conduction and valence band of the pristine polymer. As the concentration of the dopant in the PCDM film increases, the energy band gap decreases due to the formation of new energy bands associated with the polaron and bipolaron states (refer to figure 2.14)



Figure 2.14: The formation of new polaron / bipolaron bands (new bandgap).

The actual band gap of the pristine PCDM might be much broader than the 1.79 eV [3] and 1.38 eV [12] quoted above. These two band gap values are more likely to apply to the highly doped polymer with its associated bipolaron and polaron levels.

2.2.2 P3HT

Since the first synthesis of regioregular, head-to-tail, poly(3-alkylthiophene) by McCullough et al in 1995 [13], much research has been undertaken to commercialize poly(3-hexylthiophene) based devices such as field-effect transistors (FET) [14-18], light-emitting diodes (LED) [19], thin-film transistor (TFT) [20-22], solar cells [23, 24] and integrated circuits (IC) [25]. Poly(3-hexylthiophene) (P3HT) is a thiophene-

based polymer with a six carbon alkyl side-group at the third carbon in the main thiophene ring (figure 2.15).



Figure 2.15 Molecular structure of the 3-hexylthiophene trimer unit in the P3HT chain [9].

The availability of highly regioregular P3HT has simplified device fabrication, since this polymer is highly oriented when the polymer solution is spin-coated onto suitable substrates. Figure 2.16 shows the arrangement of the regioregular P3HT on such a substrate.



Figure 2.16 Two layers of the regionegular P3HT units prepared by spin-coating [26].

The conjugated polymer P3HT is a well known p-type semiconductor [27-34] with a HOMO and LUMO level at 5.20 eV and 3.53 eV respectively [35] and with a dielectric constant of 3.24 [36]. Therefore a metal with higher workfunction such as Au with a workfunction of 5.1 eV [37] and ITO with a workfunction of 4.8 eV [38] form an ohmic contact with P3HT [27, 28, 32, 39, 40, and 41]. Conversely, a metal with low workfunction such as Al, $\phi_m = 4.2eV$ [38] forms a Schottky contact with

P3HT [32, 39]. There are many reports of Schottky diodes fabricated from P3HT in the literature [27, 41, 42-46]. The hole mobility P3HT is comparable to that of amorphous silicon, i.e. μ ~0.1 cm²V⁻¹S⁻¹ with on/off ratios in Schottky diode exceeding 10⁶ [47].

2.3 Charge Transport in Semiconducting Polymer

2.3.1 Introduction

Charge is transported in conducting polymers by three different entities, namely polarons, bipolarons, and solitons. Solitons can only be created in a polymer with a degenerate ground state such as polyacetylene, while in non-degenerated polymers such as P3HT and PCDM, only polarons and bipolarons can be created. These entities are formed upon doping as discussed in section 2.2. However, in a metal/polymer/metal device, the charge has to be injected from the metal into the polymer before it can be transported through the polymer film. So, the conduction current in such a device is controlled by two basic processes: (i) injection of charge from metal to polymer, and (ii) transport of charge through the polymer bulk.

In the following, by way of background, is given a brief introduction to polarons, bipolarons and solitons followed by a discussion of the metal-semiconductor interface and finally charge transport mechanisms in semiconducting polymers.

2.3.2 Polarons, bipolarons and solitons

As mentioned earlier, polarons, bipolarons, and solitons are entities that are created upon polymer doping. In figure 2.17, the oxidative doping of polypyrrole (PPy) is used to facilitate our explanation of polarons and bipolarons. When an electron acceptor is added to the PPy, the electron is removed from the π -system of the backbone producing a free radical and a spinless positive charge.

The radical and the cation are bound together by the quinoid sequence and at this particular site, the chemical chain deforms. The deformed chain and the free radical constitute a polaron. The formation of the polaron creates new localised electronic state in the energy gap, with lower energy states being occupied by a single unpaired electron, so that the polaron has a spin of $\frac{1}{2}$. Upon further oxidation, the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. If the doping is increased further, the bipolarons will eventually form a continuous band in the polymer energy gap as shown in the energy band diagram in figure 2.14.



Figure 2.17 The formation of a polaron and a bipolaron during the oxidative doping of PPy. The positive sign is the cation and the black dot is the free radical. (Adapted from Čabala et al [48]).

The above mechanisms occur only in conjugated polymers with a non-degenerate ground state. For conjugated polymers with a degenerate ground state, the mechanism is slightly different. Basically, polarons and bipolarons are produced during oxidative doping, however due to the fact that the ground state of such polymers are twofold degenerate, the charged cations are not bound to each other by the higher energy of the quinoid configuration and can freely move along the chain. Such entities are called solitons and the oxidation of trans-polyacetylene (t-PA) is a good example of soliton formation (see figure 2.18).



Figure 2.18 The formation of soliton on the t-PA chain. (i) neutral chain, (ii) polaron, and (iii) soliton.

When an electron acceptor is added to the t-PA, an electron is removed from the chain to form a polaron. Upon further doping, the formation of a bipolaron might be expected. However, due to the degenerate nature of the ground state of this polymer, the bipolaron is unstable and the charges are free to move away from each other along the chain. As a result, the charged defects are independent of one another and can form domain walls that separate two phases of opposite orientation but identical energy. These domain walls are called solitons and can sometimes be neutral (S0) and with spin ½. A second electron might occupy or leave the soliton level, resulting in a negatively charged soliton (S-) or positively charged soliton (S+) both of which are spinless. Solitons produced in t-PA are believed to be delocalised over about 14 CH units with the maximum charge density next to the dopant counterion [9].

A polaron, bipolaron and soliton can move along the chemical chain as a unit. When these units move along the chain, the atoms along the path change their position and as a result, the chain deformation also travels along these units. A soliton has a distinctive character compared to the polaron and bipolaron. Solitons are divided into two types depending on the direction of the formation of the soliton chains. The main chain is known as the soliton and the chain with opposite direction known as the antisoliton. These two types of soliton must alternate in the chemical chain [49]. Johansson and Stafström [50] have studied how a polaron migrates through the polymer lattice, i.e. the situation in which a polaron reaches a chain end and is scattered to the surrounding chains. They employed the well-known Su-Schrieffer-Heeger (SSH) model with an additional part to include the electric field, E, and found that the polaron movement in the polymer was highly dependent on the electric field. The polaron moves with constant velocity along the chain when $E \leq 8$ MV/m with too little energy to jump to the neighbouring chain and so becomes localised at the end of the chain. When $10 \le \le 30$ MV/m, the polaron moves along the chain and is able to jump to the neighbouring chain and continue to move along this second chain. When E>30 MV/m, the polaron is totally delocalised.

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2.3.3 Metal-Semiconductor Interface

2.3.3.1 Introduction

The metal-organic semiconductor contact is generally treated in a similar manner to the metal-inorganic semiconductor. Therefore, in this section we base our discussion on the conventional theory of metal-semiconductor contacts. Contacts can behave either as a blocking (rectifying) or Ohmic depending on the characteristics of the interface. The factors that determine whether the metal-semiconductor contact is rectifying or Ohmic are the workfunction of the metal (ϕ_m) and the Fermi level (E_{Fs}) of the semiconductor. For n-type semiconductors, E_{Fs} is situated near the conduction band, whereas, for a p-type semiconductor, E_{Fs} is close to the valence band [51]. Therefore, metals with $\phi_m > E_{Fs}$ make a rectifying contact with n-type semiconductors and an Ohmic contact with p-type semiconductors. When $\phi_m < E_{Fs}$ the reverse is true as indicated in table 2.3.

Table 2.5 Electrical nature of an ideal metal-semico	onductor contact.
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Condition	n-type semiconductor	p-type semiconductor	
$\phi_m > E_{Fs}$	Rectifying	Ohmic	
$\phi_m < E_{Fs}$	Ohmic	Rectifying	

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Figure 2.19 shows the band diagram of a metal of work function ϕ_m , and an n-type semiconductor of work function (ϕ_s) immediately after contact and before charge diffusion occurs across the contact to bring the junction into thermal equilibrium. The barrier height, ϕ_B , is defined as the potential difference between the Fermi energy of the metal and the lowest unoccupied molecular orbital (LUMO) of the polymer (semiconductor). From Figure 2.19 the barrier height between the metal and the semiconductor is given by:

$$\phi_B = \phi_m - \chi_s \tag{2.1}$$

where χ_s is the electron affinity of the semiconductor.



Figure 2.19: Energy band diagram of the metal and the semiconductor immediately after the contact.

For p-type material, the barrier height is given by the difference between the highest occupied molecular orbital (HOMO) in the semiconductor and the Fermi energy in the metal:

$$\phi_B = E_g/q + \chi_s - \phi_m \tag{2.2}$$

where E_g is the energy gap between HOMO (E_v) and LUMO (E_c) in the semiconductor.

2.3.3.2 Interface Barriers at Blocking Contacts

The flat-band diagram shown in Figure 2.19 is not a thermal equilibrium diagram, since the Fermi energy in the metal is lower than that in the semiconductor. Therefore, electrons will diffuse across the interface from the semiconductor into the metal. Figure 2.20 illustrates the formation of the rectifying barrier (better known as a Schottky barrier) under thermal equilibrium. Figure 2.20 (a) shows the energy-band diagram of an n-type semiconductor with work function less than that of the metal when both the metal and semiconductor are neutral and isolated. If a wire connects the metal and semiconductor electrically, electrons in the n-type semiconductor, a positive charge, due to the ionised donor atoms stays behind. This charge creates a negative field and lowers the band edges of the semiconductor. Because the donor concentration is many orders of magnitude less than the concentration of electrons in the metal, the uncompensated donors occupy a layer of appreciable thickness, w (Figure 2.20 (b)).

The difference V_i between the electrostatic potentials outside the surfaces of the metal and semiconductor is given by $V_i = \delta \varepsilon_i$, where δ is their separation and ε_i the field in the gap. If the metal and semiconductor approach each other, V_i must tend to zero if ε_i is to remain finite (Figure 2.20 (c)).



Figure 2.20 Formation of a Schottky barrier between metal and semiconductor (a) neutral and isolated, (b) electrically connected, (c) separated by a narrow gap, (d) in perfect contact. + denotes donor ion and o denotes electrons in the conduction band.

Electrons flow into the metal until equilibrium is reached between the diffusion of electrons from the semiconductor into the metal and the drift of electrons caused by the field created by the ionised impurity atoms. This equilibrium is characterized by a constant Fermi energy throughout the structure (Figure 2.20 (d)). At thermal equilibrium, i.e. with no external voltage applied, there is a region in the semiconductor close to the junction, which is depleted of mobile carriers and is known as a depletion region with width of w (figure 2.20). The potential across the semiconductor equals the built-in potential, ϕ_i .

2.3.3.3 Ohmic Contact

An ohmic contact refers to the contact between a metal and a semiconductor that allows carriers to flow easily in and out of the semiconductor. An ideal ohmic contact must have no effect on device performance, i.e., it must be capable of delivering the required current with no voltage drop between the semiconductor and metal. In real life, therefore, an ohmic contact must have a contact resistance that is negligible in comparison to the bulk or spreading resistance of the semiconductor.

There are three approaches to achieve an ohmic contact. Firstly, a low resistance contact to a semiconductor is obtained if the barrier height is small compared to kT. Carriers can flow over the barrier in either direction without much impediment. For example, ohmic contacts are obtained for $\phi_m < \phi_s$ for n-type semiconductor and $\phi_m > \phi_s$ for p-type semiconductor. Secondly, steps can be taken to deliberately increase interface states thus reducing contact resistance by causing space-charge recombination to dominate. Lastly, an ohmic contact also can be achieved when the depletion region of the contact barrier is thin enough to allow the carriers to tunnel through the associated barrier as shown in figure 2.21.



Figure 2.21 The depletion region of the contact barrier becomes narrower by the accumulation of dopant at the metal-semiconductor interface.

When the doping level is low, only electrons that are energetic enough can surmount the energy barrier by thermionic emission (usually small numbers). As doping increases, the depletion width and the width of the barrier systematically decrease. When doping density exceeds about 10^{17} cm⁻³, significant tunnelling can take place through the thin upper region of the barrier. When doping density exceeds 10^{19} cm⁻³, the entire barrier becomes so narrow that even low energy electrons can freely tunnel through the barrier [52].

2.3.4 Charge Injection and Transport.

2.3.4.1 Introduction

Before the charge carriers can be injected into the polymer, they have to overcome a potential barrier at the metal-semiconductor interface. The potential barrier height (ϕ_B) is determined by the difference between ϕ_m and ϕ_s . Figure 2.22 illustrates a typical metal-semiconductor interface under thermal equilibrium. The potential barrier coupled with the temperature determines the carrier injection mechanism, therefore in this section the discussion is divided into three parts; (i) potential barrier approaching zero (normally ohmic contact), (ii) low potential barrier and (iii) high potential barrier.



Figure 2.22 Metal-semiconductor energy band diagrams under thermal equilibrium.

2.3.4.2 Potential Barrier Approaching Zero

When the metal-semiconductor contact is ohmic i.e. there is no effective barrier to carrier injection, the current-voltage relation is linear at low bias. So with an ohmic contact, the log-log plot between the current density and voltage at low voltages should yield a straight line with a slope of 1, and the behaviour is described by Ohm's law i.e.,

$$J = nq\mu \frac{V}{d}$$
(2.6)

where, J is the current density, n is the electron concentration, q is the charge of an electron, μ is the mobility, V is the applied voltage and d is the thickness. Equation 2.6 also can be used to describe the conduction mechanism for a trap free semiconductor with a single mobile carrier. This condition ceases to apply when the bias exceeds the space charge limit. At this limit the field due to the charge carriers dominates over the field due to the applied bias. The resulting space charge limited current (SCLC) obeys the simple form of Child's law [53],

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r \mu \frac{V^2}{d^3}.$$
 (2.7)

Here, ε_0 is the permittivity of free space and ε_r is the relative permittivity of the semiconductor.

2.3.4.3 Low Potential Barrier

In the presence of a contact barrier, at thermal equilibrium and for zero applied bias, there is no net electron flow from either metal or semiconductor, so $J_{sm} = J_{ms}$ (figure 2.22). In forward bias, the potential barrier, ϕ_i , seen by the electron in the semiconductor is reduced, hence more electrons flow from semiconductor to the metal. The barrier seen by electrons in the metal is unchanged so the electron current, $J_{sm} > J_{ms}$. Therefore as a result of the net flow of electrons from semiconductor to the metal, there is current flow under forward bias condition, J_F , given by;

$$J_F = J_0 \exp\left(\frac{qV_F}{nkT}\right) \tag{2.3}$$

where, q is the electronic charge, T is the absolute temperature, k is Boltzmann's constant, n is the ideality factor (n=1, for an ideal Schottky diode) and J_0 is the reverse saturation current.

On the other hand, under reverse bias conditions, the potential barrier, ϕ_i , seen by electrons in the semiconductor increases. Therefore more energy is needed for electrons to flow from the semiconductor to the metal. Meanwhile the potential barrier as seen by the electrons in the metal remains unchanged and so does the number of electrons flowing from metal to the semiconductor. Under reverse bias therefore, the electron current $J_{sm} < J_{ms}$, and there is a net flow of electrons from metal to the semiconductor. However, since $\phi_m >> kT$, the current flow is almost negligible and independent of the applied voltage.

When the potential barrier is small or the temperature is high, a large number of charge carriers will have sufficient energy to overcome the barrier. In this case, the charge carrier injection mechanism is determined by the semiconductor mobility. Figure 2.23 illustrates charge carrier injection from the metal into the semiconductor for both a high and low mobility semiconductor. For the case of high mobility

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semiconductors, the injected carrier will easily move away from the interface (see figure 2.23 (a)).



Figure 2.23 Charge carrier injection at a metal-semiconductor junction; (a) high mobility semiconductor, and (b) low mobility semiconductor.

Therefore the injection current is solely controlled by thermionic emission and the current density, J_0 is given by [52];

$$J_0 = A * T^2 \exp\left(\frac{-q\phi_B}{kT}\right)$$
(2.4)

where, A^* is the modified Richardson constant and ϕ_B is the difference between the Fermi level of the metal and the conduction band of the semiconductor. Basically in this case, the injection current only depends on the charge carrier injection rate. On the other hand, in low mobility semiconductors, carrier flow rate in the semiconductor is low (see figure 2.23 (b)). As a result, a back-diffusion will occur due to the large concentration of carriers that accumulate at the metal-semiconductor interface. The carrier velocity through the bulk semiconductor is proportional to the semiconductor mobility. So in this case, the injection current is determined by a combination of the number of injected carriers and the mobility of the bulk semiconductor. Therefore the current density J_0 is given by the diffusion-limited thermionic emission theory as,

$$J_{0} = q N_{c} \mu E_{\max} \exp\left(\frac{-\phi_{B}}{kT}\right)$$
(2.5)

where, N_C is the effective density of states in the conduction band and E_{max} is the maximum field strength in the space charge layer occurring at the metal-semiconductor interface and proportional to $(\phi_i - V)^{1/2}$.



Figure 2.24 Image-force lowering of metal-semiconductor interface barrier.

When thermionic emission dominates and at low electric fields, when the slope $\ln(J)$ versus $\ln(V)$ is approximately 1, this region is considered to be the ohmic region [54]. Above the ohmic region, the current density follows the Richardson-Schottky emission model (see equation 2.4). This model however is only valid at lower fields and higher temperatures. At higher fields, the metal workfunction for thermionic emission is reduced thus lowering the effective barrier height. This phenomenon is known as image force lowering and is understood with the aid of figure 2.24.

In figure 2.24, the image potential and the applied potential are shown together with the resultant barrier which represents an effective lowering of the image barrier by an amount $\Delta \phi$. An electron leaving a metal will induce a positive charge density at the metal surface to screen its electrostatic field. This screening effect can be represented by an image charge of the electron located at the same distance behind the metal surface. The attractive force, F, between the electron in the semiconductor and the equal positive charge in the metal is given by [52],

$$F = \frac{-q^2}{4\pi (2x)^2 \varepsilon_0 \varepsilon_r} = \frac{-q^2}{16\pi \varepsilon_0 \varepsilon_r x^2}$$
(2.6)

where, ε_0 and ε_r are the permittivity of the free space and relative permittivity respectively. The potential energy $\phi(x)$ of an electron at a distance x from the metal surface is given by,

$$\phi(x) = -\int_{\infty}^{x} F dx = \frac{q^2}{16\pi\varepsilon_0\varepsilon_r x}$$
(2.7)

for x > 0, so that the electron is positioned in the semiconductor rather than in the metal. The resulting image potential energy of an electron (or hole in the case of hole injection) as measured from vacuum level is;

$$\phi(x) = \frac{q^2}{16\pi\varepsilon_0\varepsilon_r x} + qEx \,. \tag{2.8}$$

The interaction between electrostatic and image force potential results in a barrier whose maximum is situated at x_0 , where,

$$x_{0} = \left(\frac{q}{16\pi\varepsilon_{0}\varepsilon_{r}E}\right)^{\frac{1}{2}}.$$
(2.9)

The barrier lowering, $\Delta \phi$, is readily shown to be given by,

$$\Delta \phi = \left(\frac{qE}{4\pi\varepsilon_0\varepsilon_r}\right)^{\frac{1}{2}}.$$
(2.10)

Taking into account the image force lowering, the Richardson-Schottky thermionic emission equation is modified to;

$$J = A * T^{2} \exp\left(\frac{q\beta E^{\frac{1}{2}} - \phi}{kT}\right)$$
(2.11)

where, the barrier lowering coefficient, $\beta = \left(\frac{q^3}{4\pi\varepsilon_0\varepsilon_r}\right)^{\frac{1}{2}}$. At a rectifying Schottky

contact, the field appearing at the contact is the sum of the applied field and that of the ionised dopants in the depletion region. Thus the reverse current is given by,

$$J_{R} = J_{0} \exp\left[\left(\frac{q}{kT}\right)\left(\frac{q^{3}N_{D}(V_{C} - V_{A})}{8\pi^{2}\varepsilon_{\infty}^{2}\varepsilon_{s}\varepsilon_{0}^{3}}\right)^{\frac{1}{4}}\right]$$
(2.12)

where, N_D is the donor density, V_A is the applied voltage, ε_{∞} and ε_s , are the high frequency and static relative permittivities respectively and $V_c = \phi_i - (kT/q)$. The reverse current is now seen to vary as $(V_c - V_A)^{\frac{1}{4}}$.

2.3.4.4 High Potential Barrier

Up to this point we have assumed that the potential barrier is relatively low and the temperature is relatively high. However, when the temperature decreases or the

potential barrier becomes very high, the number of charge carriers that can overcome the potential barrier falls so that thermionic emission becomes insignificant. Carrier injection then can only occur via quantum mechanical tunnelling through the potential barrier. The charge carrier is assumed to tunnel from the metal through a triangular barrier to the empty states at the LUMO or HOMO. Alternatively, the tunnelling might occur from the metal to empty localised states if the polymer is heavily doped.

The tunnelling current, I_t , is obtained from the product of the carrier charge, its velocity and density as described by Fowler-Nordheim tunnelling theory as [55, 56], i.e.

$$I_t = qAv_t n\Theta.$$
(2.13)

The tunneling velocity, v_t , equals the Richardson velocity or the average velocity with which the carriers approach the barrier. The carrier density *n*, is the density of electrons available for tunnelling. For a triangular barrier, the tunnelling probability, Θ , is given by [52],

$$\Theta = \exp\left(-\frac{4\sqrt{2qm^*}}{3hE}\phi_b^{\frac{3}{2}}\right)$$
(2.14)

where, m^* is the effective mass of the electrons, h is Planck's constant, and E is the electric field. The tunnelling current therefore depends exponentially on the barrier height, ϕ_b , to the power of 3/2.



Figure 2.23 Electron tunneling through the barrier according to the Fowler-Nordheim theory.

Hence, in order to relate the tunnelling current to the applied field (E), equation 2.13 can be rewritten as [57],

$$I = KE^2 \exp\left(-\frac{\kappa}{E}\right) \tag{2.15}$$

where,

$$\kappa = \frac{8\pi\sqrt{2m^*}}{3qh}\phi_b^{3/2}.$$
 (2.16)

Parker [58] employed the Fowler-Nordheim tunnelling theory to analyse hole injection in an ITO/MEH-PPV/Ca device in which polymer layer was 120 nm thick. From the linear part of the $\ln(I/E^2)$ versus 1/E plot, they estimated the barrier height at the metal-semiconductor interface to be 0.2 eV.

2.3.5 Charge Transport in Disordered Organic Semiconductors

Carrier mobility in organic crystals such as pentacene is lower than crystalline silicon (see table 2.2) mainly due to the fact that molecules in organic crystals are held together by weak van der Waals forces. As a result, the valence and conduction bands are narrow and the band structure is easily disrupted by introducing disorder in the system. Although organic molecular crystals can show band conduction, excitations and interactions of localised individual molecules become dominant. On the other hand, in conjugated polymers, the well-ordered structural configuration of a crystal is absent and the conjugation of the polymer backbone is disrupted by chemical or structural defects, such as chain kinks or twists.

The description of charge transport processes in a disordered polymer semiconductor in terms of a standard semiconductor model is not as simple therefore. This is due to the absence of an ideal three-dimensional lattice structure in a disordered polymer semiconductor. The concept of band conduction by free charges does not apply and instead the formation of localised states is enhanced and a different theoretical approach is required. This has led to the emergence of several charge transport models for organic semiconductor systems with some models showing good agreement with electrical measurement for some particular systems. However, there is no complete solution available due to the diversity and complexity of disordered organic semiconductor systems.

Among the models proposed, Bässler [59] derived a charge transport model especially for disordered organic systems in 1993. In this model, electron-phonon

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coupling was assumed to be weak, so that polaronic effects can be neglected and the energy variation should be similar to the variations found in excitonic adsorption and fluorescence bands. In addition, the energy variations are also affected by variations in the conjugation length of the polymer backbone and the presence of defects on the chemical chain. Charge carriers are assumed to hop between sites in a regular array and the hopping rate is affected by the chain disorder. With negligible polaronic effects, the energy levels of the HOMO and LUMO are not discreet but rather distributed around the average energy level with a Gaussian shape distribution as shown in figure 2.24.



Figure 2.24 Representation of the energy distribution of localised states which is approximated by a Gaussian distribution for LUMO and HOMO.

This energy variation is termed the site energy variation and is also known as *diagonal disorder*. The distribution of site energies $\rho(E)$ is given by [59];

$$\rho(\mathbf{E}) = \left(2\pi\sigma^2\right)^{-\frac{1}{2}} \exp\left(-\frac{\mathbf{E}^2}{2\sigma^2}\right)$$
(2.17)

where σ is the variance. In addition, the hopping rate is also affected by another disorder known as *off-diagonal disorder*, ODD. This disorder is due to the variations in the intersite coupling as a result of the randomisation of the chain orientation and the distance between hopping sites. Therefore the hopping rate is described by a Gaussian attached to each site with a variance Σ .

Monte Carlo simulations and experimental data were employed by Bässler [59] to derive an approximate formula for the temperature, T and field, E, dependence of mobility, μ , which is given by,

$$\mu(\sigma, \Sigma, E, T) = \mu_0 \exp\left[-\left(\frac{2\sigma}{kT}\right)^2\right] \times \begin{cases} \exp\left[C\left(\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right)\sqrt{E}\right] - \dots - for \ \Sigma \ge 1.5\\ \exp\left[C\left(\left(\frac{\sigma}{kT}\right)^2 - 2.25\right)\sqrt{E}\right] - \dots - for \ \Sigma < 1.5 \end{cases}$$

$$(2.18)$$

where, C is a constant that depends on the site spacing, $(C=2.9 \times 10^{-4} (\text{cmV}^{-1})^{1/2})$, μ_0 is the mobility in the limit $T \to \infty$, σ and Σ are the variances for *diagonal* and *off-diagonal disorder* respectively.

As clearly shown in equation 2.18, the mobility μ depends on the field *E*, but the effect is only measurable when $E > 10^4$ V/cm. The problem of the field-dependent mobility was resolved numerically by Murgatroyd [60] assuming a Poole-Frenkel (P-F) type dependency of μ on *E*;

$$\mu(E) = \mu_0 \exp(\beta \sqrt{E}). \tag{2.19}$$

Typically, β turns out to be lower by a factor of 2.5 to 3 than the value predicted by the P-F theory for field-assisted lowering of coulombic energy of an electron-cation pair, which predicts that $\beta = (q^3/\pi\varepsilon_0\varepsilon_r)^{\frac{1}{2}}$ [61]. In the P-F model, when the field was applied the transfer rate between sites increases due to the modification of the coulomb potential near a localised charge. On the other hand, in the Bässler model, when the field was applied, the level of positional disorder, Σ , increases which accounts for the local variation of the intersite distance which takes place in a disorder medium. Basically these two models are equivalent to each other as long as the temperature is assumed to be constant and the value of β is appropriately estimated.
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3.1 Introduction

In this chapter basic device concepts are presented to provide a foundation for the discussion of the results presented in Chapters 5 and 6. The Schottky diode is first discussed in section 3.2 followed by the metal-insulator-semiconductor (MIS) structure in section 3.3. Finally the principles underlying the operation of memory devices are discussed in section 3.4 with special attention paid to the floating gate memory device.

3.2 Schottky Diode

The Schottky diode uses a metal-semiconductor junction for rectification instead of a semiconductor-semiconductor junction as in conventional p-n diodes. Schottky diodes are unipolar devices, i.e. they do not inject minority carriers into a neutral region, as do PN diodes. Since there is no minority charge storage, the turn-off event is fast, and the transient reverse current is small. As a result, the switching energy dissipated during turn-off is minimal i.e. low forward voltage drop. A typical polymer Schottky diode is illustrated in figure 3.1, with the depletion region created at the polymer/Al interface.



Figure 3.1 Polymer Schottky diode configurations.

3.2.1 Depletion Layer

As discussed in section 2.3.3.2, the depletion of the mobile carriers at the metalsemiconductor interface as shown in figure 2.20 (d) creates a region known as the depletion region. In thermal equilibrium, the conduction and valence bands of the semiconductor are brought into a definite energy relationship with the Fermi level in the metal. Suppose figure 3.2 represents the band diagram of an ideal Schottky barrier with an n-type semiconductor.



Figure 3.2 Depletion region width of the Schottky barrier under different reverse bias voltages, (a) V_r and (b) $V_r + \Delta V_r$.

In figure 3.2, the conduction and valence band edges in the semiconductor under a reverse bias (a) and the barrier for a larger reverse bias (b). As clearly illustrated in figure 3.2, as the reverse bias increases from V_r to $V_r + \Delta V_r$, the electrons in the conduction band of the semiconductor move further away from the metal-semiconductor interface and the depletion region increases from w to $w + \Delta w$. The depletion width associated with such a metal-semiconductor barrier can be calculated from the equation [1]:

$$w = \sqrt{\frac{2\varepsilon_s}{qN_D}(\phi_i - V - \frac{kT}{q})}$$
(3.1)

where, ε_s is the permittivity of the semiconductor, q is the electronic charge, N_D is doping density, V is the applied voltage, k is Boltzmann constant and T is the absolute temperature in Kelvin. The change in depletion region produced by the voltage change, also results in a change in the charge stored in the depletion region and hence gives rise to the barrier capacitance. The space charge Q_{sc} per unit area of the semiconductor and the depletion layer capacitance C per unit area are related by the equations [1]:

$$Q_{sc} = qN_D w = \sqrt{2q\varepsilon_s N_D(\phi_i - V - \frac{kT}{q})}$$
(3.2)

$$C = \frac{\left|\partial Q_{SC}\right|}{\partial V} = \sqrt{\frac{q\varepsilon_s N_D}{2(\phi_i - V - \frac{kT}{q})}} = \frac{\varepsilon_s}{w}.$$
(3.3)

Thus the Schottky barrier capacitance is seen to depend on the applied voltage. Therefore, by rearranging equation (3.3) to

$$C^{-2} = \frac{2}{q\varepsilon_s N_D} \left[\phi_i - V - \frac{kT}{q} \right]$$
(3.4)

it is seen that doping density, N_D , and built-in potential, ϕ_i , can be obtained from the plot C^2 versus V. If N_D is constant throughout the depletion region, the plot of C^2 versus V should produce a straight line as shown in figure 3.3. In this case, the slope of the straight part of the graph in figure 3.3 can be used to calculate N_D and $V_R = \phi_i$ when $C^2 = 0$. On the other hand, the differential capacitance method (equation 3.5) can be used to establish the doping profile throughout the depletion region if N_D is not constant, since equation 3.3 can also be rewritten as;

$$-\frac{d(C^{-2})}{dV} = \frac{2}{q\varepsilon_s N_D}.$$
(3.5)

Therefore,

$$N_D = \frac{2}{q\varepsilon_s} \left[-\frac{1}{d(C^{-2})/dV} \right].$$
(3.6)



Figure 3.3 Theoretical plot of C^2 versus V (reverse bias) for an ideal Schottky diode formed from an n-type semiconductor.

3.2.2 AC Behaviour of an Ideal Schottky Diode

The previous section has concentrated on the capacitance, C_d , of the depletion region only. However, a Schottky diode consists of two different regions; the high resistivity depletion region and a low resistivity bulk region [2, 3]. In polymer devices, the resistivity of the bulk is not sufficiently low to ignore as is the case for silicon. While the small signal capacitance and Mott-Schottky relations (equation 3.3 and 3.4) still apply to the depletion region the measured capacitance is modified by the presence of the bulk region. The effect of the bulk is readily modelled by the equivalent circuit in figure 3.4



Figure 3.4 Equivalent circuit of an Ideal Schottky diode.

where C_d and R_d represent the capacitance and the resistance of the depletion region, and C_b and R_b represent the capacitance and resistance of the bulk region. In this section, based on the work by Taylor and Gomes [2], we will briefly discuss the frequency-dependence of the total admittance, Y_p , of the circuit in figure 3.4, where

$$Y_p = G_p + j\omega C_p. \tag{3.7}$$

Here C_p is the equivalent parallel capacitance which is given by,

$$C_{p} = C_{g} + \frac{C_{LF} - C_{g}}{1 + (\omega \tau_{R})^{2}}$$
(3.8)

and G_p is the parallel conductance given by,

$$G_{p} = G_{LF} + \frac{G_{a}}{1 + (\omega \tau_{R})^{2}}.$$
(3.9)

 C_g is the series sum of the depletion layer and bulk capacitances and can be written as,

$$C_g = \frac{C_d C_b}{(C_d + C_b)} \tag{3.10}$$

while C_{LF} , the effective low frequency capacitance, is readily deduced to be,

$$C_{LF} = \frac{C_d R_d^2 + C_b R_b^2}{(R_d + R_b)^2}.$$
(3.11)

 G_{LF} is the low frequency or DC conductance, i.e.

$$G_{LF} = \frac{1}{\left(R_d + R_b\right)} \tag{3.12}$$

while G_a is the AC conductance and given by,

$$G_{a} = \frac{\omega^{2} R_{d} R_{b} (C_{d} R_{d} - C_{b} R_{b})^{2}}{(R_{d} + R_{b})^{3}}.$$
(3.13)

Finally, the circuit relaxation time, τ_R is given by,

$$\tau_R = \frac{R_d R_b \left(C_d + C_b\right)}{R_d + R_b}.$$
(3.14)

Therefore, the circuit follows a classic Debye-like relaxation [4] with a single relaxation time and at low frequency, so long as $R_d \gg R_b$ then $C_p \sim C_d$, $G_p \sim R_d^{-1}$ and $\tau_R \cong R_b (C_d + C_b)$. If $R_d C_d \gg 1$ then the loss tangent (tan δ) which reaches a maximum value of tan δ_{max} at a frequency, v_{max} , is obtained from equations 3.15, 3.16, and 3.17 i.e.

$$\tan \delta = \frac{\omega C_d R_b}{1 + (\omega R_b)^2 (C_d + C_b) C_b},$$
(3.15)

$$\tan \delta_{\max} = \frac{1}{2} \left(\frac{C_d^2}{(C_d + C_b)C_b} \right)^{\frac{1}{2}}$$
(3.16)

and

$$v_{\max} = \frac{1}{2\pi R_b} \left(\frac{1}{(C_d + C_b)C_b} \right)^{\frac{1}{2}}.$$
 (3.17).

Figure 3.5 illustrates the theoretical plot of the capacitance and loss of the circuit in figure 3.4 as a function of frequency. From figure 3.5, the capacitance is practically constant at low frequencies but as the frequency increases, the measured capacitance decreases from its low frequency value (see figure 3.5). At low frequencies, where $\omega \tau_R \ll 1$, the bulk resistance (R_b) dominates the semiconductor response since the

reactance, $1/j\omega C$, of the bulk capacitance (C_b) is very high, and the measured capacitance corresponds to the depletion region capacitance, C_d . As the frequency increases toward the relaxation frequency, i.e. $\omega \tau_R \approx 1$, and the reactance of C_b approaches R_b , the contribution of C_b to the device capacitance becomes more significant. Therefore, the dispersion due to the bulk region starts to appear (~10 – 100 kHz).

At sufficiently high frequencies, where $\omega \tau_R >> 1$, the reactance of C_b decreases sufficiently, so that it dominates R_b . At these higher frequencies, the loss (G/ω) also decreases because majority carriers are unable to follow the applied signal.



Figure 3.5 Theoretical plot of (a) capacitance and (b) loss (G/ω) versus frequency of the circuit in figure 3.4, and for component values of C_d =450 pF, C_b =250 pF, R_d =1.5 x 10⁸ Ω , and R_b =8000 Ω .

The semiconductor now behaves as an insulator and the total capacitance C_T becomes,

$$C_T = \frac{C_d C_b}{C_d + C_b}.$$
(3.18)

The loss-frequency plot i.e. G/ω vs. frequency in figure 3.5 (b) increases rapidly as the frequency decreases due to the DC component of the conduction (G_{DC}/ω) .

In practice, it is also necessary to account for a small resistance (contact resistance) that exists at the electrode interfaces giving rise to a resistance, R_s , in series with the two main components. Thus the equivalent circuit in figure 3.4 must be modified as shown in figure 3.6 [5]. The impedance of this circuit is given by,

$$Z = \frac{1}{G_p + j\omega C_p} + R_s.$$
3.19



Figure 3.6 Equivalent circuits for a diode with small series resistance, R_s .

Equations (3.7) may now be re-derived to yield a total admittance, Y_T , given by,

$$Y_T = \frac{G_P + j\omega C_P}{1 + R_s G_P + j\omega C_P R_s}.$$
(3.20)

After expanding and rearranging equation (3.20), yields;

$$Y_T = \frac{G_p (1 + R_s G_p) + \omega^2 C_p^2 R_s + j \omega \{ (C_p (1 + R_s G_p) - C_p R_s G_p \}}{(1 + R_s G_p)^2 + \omega^2 C_p^2 R_s^2}.$$
 (3.21)

Therefore, total conductance, G_T , is given by,

$$G_T = \frac{G_p (1 + R_s G_p) + \omega^2 C_P^2 R_S}{(1 + R_s G_p)^2 + \omega^2 C_P^2 R_S^2},$$
(3.22)

and total capacitance, C_T , is represented by,

$$C_T = \frac{C_p (1 + R_s G_p) - C_p R_s G_p}{(1 + R_s G_p)^2 + \omega^2 C_p^2 R_s^2}.$$
(3.23)

When $\omega \rightarrow \infty$ and $G_p = R_p^{-1}$, equation (3.23) becomes;

$$C_T = \frac{C_p}{(1 + R_s G_p)^2 + \omega^2 C_p^2 R_s^2}.$$
(3.24)

Finally, now the circuit relaxation time is given by;

$$\tau_R = \sqrt{\frac{C_p^2 R_s^2}{(1 + R_s G_p)^2}} \quad . \tag{3.25}$$

In this case, a Debye-like dispersion is still expected. However C_p and G_p are now frequency dependent. If there are two well-separated processes, the relaxation time of the second dispersion at high frequency (τ_{HF}) is given by,

$$\tau_{HF} = C_p R_s \,, \tag{3.26}$$

so long as $G_p \sim 0$ and $G_{LF} \sim 0$.

The theoretical frequency response of the circuit with a small series resistance is similar to figure 3.5, except that a second dispersion is also observed at high frequency as shown in figure 3.7.



Figure 3.7 Theoretical plots of (a) capacitance and (b) loss (G/ω) versus frequency of the circuit in figure 3.6 for the component values, C_d =450 pF, C_b =250 pF, R_d =1.5 x 10⁸ Ω , R_b =8000 Ω and Rs=2 Ω .

3.3 Metal-Insulator-Semiconductor Devices

3.3.1 Introduction

The semiconductor/insulator interface is one of the main factors determining the reliability and stability of many semiconductor devices. Therefore an understanding of the surface physics with the help of an appropriate tool is of great importance when seeking to improve device operation. The Metal-Insulator-Semiconductor (MIS) structure is such a tool and has been widely employed to study the semiconductor-insulator interface.

3.3.2 Ideal MIS Capacitor

The MIS capacitor consists of a Metal-Insulator-Semiconductor structure as illustrated in figure 3.6. Shown is the semiconductor substrate with a thin insulator layer and a top metal contact, also referred to as a gate, which should be a perfect blocking contact provided the insulator used has good insulating properties. A second metal layer forms an Ohmic contact to the back of the semiconductor. In an ideal MIS diode at zero applied bias, the energy difference between the metal work function, ϕ_m , and the semiconductor work function, ϕ_s , is zero. Furthermore, the only charges that can exist in the structure under any biasing conditions are those in the semiconductor and those of opposite sign on the metal surface adjacent to the insulator. Finally, there is no carrier transport through the insulator under dc biasing conditions, i.e. the resistivity of the insulator is infinite.



Figure 3.6 Metal-insulator-semiconductor (MIS) capacitor.

Figure 3.7 shows the band diagram of such an ideal MIS structure formed on an ntype semiconductor without applied bias. From the properties of the ideal MIS structure, the work function difference between the metal and an n-type semiconductor, ϕ_{ms} , is given by,

$$\phi_{ms} = \phi_m - \left(\chi_s + \frac{E_g}{2q} - \psi_B\right) = 0 \tag{3.23}$$

where χ_s is the electron affinity of the semiconductor, E_g is the semiconductor band gap, q is the electron charge, and ψ_B is the potential difference between the bulk Fermi level E_F and the intrinsic Fermi level E_i of the semiconductor.



Figure 3.7 Energy diagram of an ideal Metal-Insulator-Semiconductor (MIS) structure with an n-type semiconductor.

From figure 3.7, the electron affinity of the insulator, χ_i , is shown as the difference between the metal workfunction, ϕ_m , and the potential barrier between the metal and the insulator, ϕ_B . The situation illustrated in figure 3.7 is also known as the flat-band condition which should occur for an ideal MIS structure in thermal equilibrium under zero bias. To understand the different bias modes of an MIS capacitor we now consider three different bias voltages corresponding to accumulation, depletion and inversion modes of operation respectively. These three modes as well as the charge distributions associated with each of them are shown in figure 3.8.



Figure 3.8 Charges distribution (top) and energy-band diagram (bottom) of an ideal Metal-Insulator-Semiconductor under (a) accumulation, (b) depletion, and (c) inversion, where a positively charged inversion layer (filled-circular) forms at the semiconductor-insulator interface in addition to the depletion layer.

For an n-type semiconductor, accumulation occurs when positive voltage is applied to the gate so as to attract electrons from the substrate to the insulator-semiconductor interface (figure 3.8 (a)). At this voltage, the bottom of the conduction band bends downward and is closer to the Fermi level. There is no current flow in an ideal MIS structure, so the Fermi level in the semiconductor remains constant. Since the carrier density depends exponentially on the energy difference ($E_C - E_F$), this band bending causes an accumulation of electrons near the insulator-semiconductor interface.

Depletion occurs when a small negative voltage is applied to the gate, the band bends upward and the negative charge on the gate repels the mobile electrons (majority carriers) into the substrate (figure 3.8 (b)). Therefore, the semiconductor is depleted of mobile carriers at the interface and a positive charge, due to the ionized donor ions remains forming the depletion or space charge region. The voltage separating the accumulation and depletion regime is referred to as the flat band voltage, V_{FB} .

When a larger negative voltage is applied to the gate inversion occurs at voltages beyond the threshold voltage (V_T) . At these voltages, the band bends upward to such an extent that the Fermi level (E_F) at the surface crosses over the intrinsic Fermi level (E_i) . In inversion, a layer of free holes accumulates at the insulatorsemiconductor interface in addition to the depletion layer as shown in figure 3.8. In strong inversion the concentration of the minority carriers (holes), at the interface exceeds the concentration of majority carriers (electrons) in the bulk. When inversion occurs, additional negative charges on the gate are balanced by charges in the inversion layer. The depletion region no longer expands and reaches a maximum width which can be estimated from the relation [1],

$$w_{\max} = \sqrt{\frac{4\varepsilon_s kT \ln \left(\frac{N_D}{n_i}\right)}{q^2 (N_D - N_A)}},$$
(3.24)

where ϵ_s represents the absolute permittivity of the semiconductor, n_i is the intrinsic carrier density and N_D and N_A are the donor and acceptor dopant densities respectively.

3.3.3 Ideal MIS Capacitance-Voltage Curves

The effects of an applied voltage discussed in section 3.3.2 can be used to derive the AC characteristics of the MIS capacitor. When a small sinusoidal AC voltage of angular frequency, ω , is superimposed on the gate bias the band bending will vary with time as it follows the alternating signal voltage. The charges on the gate will be balanced by the diffusion of charges in and out the semiconductor; hence capacitance can be associated with the structure.

Furthermore, in view of the processes occurring at the insulator/semiconductor interface (figure 3.8) the capacitance will depend on the applied voltage to reflect the three regimes of accumulation, depletion and inversion as shown in figure 3.9. In the accumulation regime, the majority carrier concentration at the interface follows the AC signal so the measured capacitance is equal to that of the insulator, i.e. $C = C_{in}$. In the depletion regime, the device capacitance, C_s decreases from its value in accumulation because now the depletion region starts to dominate the semiconductor

response to the measured capacitance. Now the measured capacitance becomes the series sum of the depletion capacitance, C_d and insulator capacitance C_{in} so that,

$$C = \frac{C_{in}C_d}{C_{in} + C_d},\tag{3.25}$$

and can be represented by the equivalent circuit in figure 3.10.



Figure 3.9 Ideal capacitance-voltage curves for a MIS structure based on an n-type semiconductor, (a) at low frequency, and (b) at high frequency.

In the inversion regime, minority carriers in the inversion layer at the semiconductor/insulator interface can give rise to two different regimes depending on whether the frequency modulating AC signal is (a) low - solid curve or (b) high - dotted curve in figure 3.9. At sufficiently low frequency (e.g. 1 Hz) the thermal generation and recombination of minority carriers can follow the AC modulation so that the measured capacitance is again equal to the insulator capacitance. At

sufficiently high frequency (e.g. 10 kHz) these processes cannot follow the modulation. Only majority carriers at the edge of the depletion region are able to do so. In this case, the measured capacitance is again equal to the series sum of the insulator and depletion capacitances. However, since the rate at which the gate voltage, Vg, is ramped is relatively slow, the depletion region capacitance remains constant.



Figure 3.10 Schematic diagram of the MIS structure couple with a simple equivalent circuit, and arrow on C_d denotes voltage dependence.

3.3.4 Maxwell-Wagner Dispersion

Up to this point, majority carriers were assumed to respond instantaneously to the AC variation. In fact, however, the response of an ideal MIS structure to a sinusoidal voltage can be modelled by the equivalent circuits in figure 3.11 [6] when the device is driven into (a) accumulation and (b) depletion modes. Here C_{in} represents the

insulator capacitance, C_d the depletion capacitance, C_b , C_b ', R_b and R_b ' the capacitance and resistance of the bulk semiconductor in accumulation and depletion mode respectively, and R_s the contact resistance.

The equivalent circuits presented in figure 3.11 will have two relaxation frequencies. The main relaxation arises when C_b or C_b ' is shunted by R_b or R_b ' respectively and the second relaxation resulting from the presence of R_s which occurs at higher frequency. In the case of well-separated dispersions, the circuit admittance, Y_P , governing the first relaxation frequency but below the secondary relaxation is given by

$$Y_P = G_P + j\omega C_P, \tag{3.26}$$

where C_P and G_P are measured values of the parallel capacitance and conductance respectively.



Figure 3.11 *MIS capacitor coupled with equivalent circuit (a) accumulation and (b) depletion with arrow indicates voltage dependence.*

However, total low-frequency device capacitance depends on whether the device was in accumulation or depletion mode. In accumulation (figure 3.11(a)), the frequency response of the capacitance and the loss, $\frac{G_p}{\omega}$ is similar to the capacitance and loss characteristics of the Schottky diode in figure 3.6 and the relaxation time, τ_R of the circuit is given by [2],

$$\tau_R = R_b (C_{in} + C_b). \tag{3.27}$$

Therefore, low-frequency capacitance in accumulation mode corresponds to the insulator capacitance, C_{in} . Furthermore, as for the Schottky diode the loss passes through a maximum at the circuit relaxation frequency given by:

$$f_{R} = \frac{1}{2\pi\tau_{R}} = \frac{1}{2\pi R_{b} (C_{in} + C_{b})}$$
(3.28)

while the measured capacitance at very high frequency is the series sum of C_{in} and C_b and given by:

$$C_p = \frac{C_{in}C_b}{C_{in} + C_b}.$$
(3.29)

When the semiconductor is driven into depletion which corresponds to the equivalent circuit shown in figure 3.11(b), equation 3.28 is still applicable in determining the relaxation frequency of the circuit. However, since the depletion region in the semiconductor now contributes significantly to the measured capacitance in the low frequency region, C_{in} must be changed to the series sum of C_{in} and C_d the depletion region capacitance. Therefore the relaxation frequency (f_R) becomes:

$$f_{R} = \frac{1}{2\pi R_{b}^{'} \left(\frac{C_{in}C_{d}^{'}}{C_{in} + C_{d}^{'}} + C_{b}^{'}\right)}$$
(3.30)

Here, R_b and C_b are the resistance and capacitance of the bulk semiconductor in the depletion mode as shown in figure 3.11(b), i.e. $R_b' = \frac{\rho_S(d_S - w)}{A}$ and $C_b' = \frac{\varepsilon_S A}{d_S - w}$, with d_S equal to the semiconductor thickness, w the depletion region width at a particular voltage, A the area of the capacitor and C_d' the depletion capacitance given by $\frac{\varepsilon_S A}{w}$. In the depletion mode, the relaxation frequency should increase as the depletion width increases from 0, where $C_d' = \infty$, to completely fill the semiconductor thickness, where $C_d' = C_b$ within the limits governed by:

$$\frac{1}{2\pi R_b \left(C_{in} + C'_d \right)} < f_R < \frac{1}{2\pi R'_b C'_b}.$$
(3.31)

For two well-separated dispersions, the second relaxation is centred at a frequency given by,

$$f_R = \frac{1}{2\pi R_S C_S} \tag{3.32}$$

where C_S is the series sum of C_{in} , C'_d and C'_b .

3.4 Memory Device

As indicated in chapter 1, there are several different approaches that can be adopted for achieving a memory device. In this thesis, we focus on (a) MOS-type devices modified to include an additional charge trapping layer in the gate insulator and (b) a device based on the Schottky diode structure. Therefore in this section semiconductor memory devices that operate in a similar manner to our target devices will be discussed.

3.4.1 Floating Gate Memory Device

When a typical MIS device is modified so that semi-permanent charge storage inside the gate insulator is possible, the new structure becomes a nonvolatile memory device. The modification is done by embedding an isolated inner gate between the external gate and the semiconductor as shown in figure 3.12. The inner gate is also known as a 'floating gate' and is the data-storing element in the memory cell. Data is stored in the cell in the form of electrical charge accumulated on the floating gate. The amount of charge stored in the floating gate depends on the voltage applied to the external gate of the memory cell which controls the flow of charge into or out of the floating gate. The data contained in the cell depends on whether the voltage of the stored charge exceeds a specified threshold voltage V_T or not.

The first memory device incorporating the floating gate was studied by Kahng and Sze [7] in 1967. The energy band diagram of this memory device based on an ntype semiconductor is shown in figure 3.13. Here, G is the external metal gate, FG is the floating metal gate, I_2 is the insulator separating G and FG, and has a thickness d_2 , and I_1 is the insulator between FG and the semiconductor and has thickness d_1 . When a positive voltage is applied to the external metal gate, $V_G > 0$, an electric field, E, is established in both insulators (figure 3.13 (a)). In this situation, the device is similar to a typical MIS device in accumulation mode, whereby the conduction band in the semiconductor bends downward and allows electrons to be transported through the first insulator layer (I_I) into the floating gate.



Figure 3.12 Basic structure of the MIS device incorporating an isolated inner gate between insulator 1 and 2.

In general, the current transport in insulators is strongly dependent on the electric field, and is more likely to be dominated by Fowler-Nordheim tunnelling or the Poole-Frenkel mechanism. Now, from Gauss's law [1], we have,

$$\varepsilon_1 E_1 = \varepsilon_2 E_2 + Q. \tag{3.33}$$

Here, ε_1 and ε_2 , and E_1 and E_2 are the absolute permittivities of insulator 1 and 2, and the electric fields across insulator 1 and 2 respectively, whereas Q is the stored charge per unit area on the floating gate. The voltage applied to the external gate will develop different voltage drops across insulator 1 and 2, which satisfy the relation,

$$V_G = V_1 + V_2 = d_1 E_1 + d_2 E_2. aga{3.34}$$



Figure 3.13 Energy band diagram of the floating gate memory device with n-type semiconductor. (a) $V_G > 0$, accumulation of the electrons in FG, (b) Electrons are stored in FG when the bias is removed and (c) $V_G < 0$, discharging of electrons from FG (after [7]).

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Now from equations 3.33 and 3.34, we can estimate the electric field across one of the insulators. For instance in I_1 , E_1 is given by,

$$E_{1} = \frac{V_{G}}{d_{1} + d_{2} \left(\frac{\varepsilon_{1}}{\varepsilon_{2}} \right)} + \frac{Q}{\varepsilon_{1} + \varepsilon_{2} \left(\frac{d_{1}}{d_{2}} \right)}.$$
(3.35)

When the external voltage is removed (figure 3.13 (b)) after a given time, assuming that $d_2 >> d_1$ the threshold voltage will shift by an amount ΔV_T given by,

$$\Delta V_T = -\frac{d_2 Q}{\varepsilon_2} \,. \tag{3.36}$$

By applying a negative voltage to the external gate, the stored electrons in the floating gate will be discharged as shown in figure 3.13 (c). For sufficiently high negative voltages, excess electrons can be ejected from the floating gate leaving it positively charged.



Figure 3.14 Shift of the C-V curve along the voltage axis due to accumulation of (a) positive charge (Q_p) and (b) negative charge (Q_n) , in the floating gate for p-type silicon (adapted from Sze [1]).

The threshold voltage shift consequent upon populating the floating gate with positive or negative charges manifests itself as a shift in the capacitance-voltage (C-V) plot. Figure 3.14 shows the shift along the voltage axis of a high-frequency C-V curve of a MOS capacitor based on p-type silicon when (a) holes and (b) electrons are accumulated in the floating gate.

3.4.2 Nano-crystal Memory Device

For the purpose of the present discussion, the term nano-crystal refers to any metallic island structure embedded in the gate insulator of a memory device and includes nano-particles, nano-clusters, quantum dots, etc. Memory devices are coming under increasing pressure to become smaller, demand less power yet store more and more data. This is important to meet the demands of a range of modern electronic devices which currently run a variety of functions within cars, mobile phones, other wireless devices and industrial controls. The increasing use of portable electronics and embedded systems has resulted in the need for low-voltage, high-density non-volatile memory devices. Nanocrystal memories, utilizing the Coulomb blockade effect in small geometries and distributed charge storage, have the potential to satisfy such a need. Basically, the energy band diagram of any nanocrystal-based memory device.

Conventional floating-gate flash memories have not been able to operate with very thin tunnel oxides because of data retention and endurance issues. Hence, it is becoming increasingly difficult to further shrink flash memory devices from their

current size. Although the insulating layer is effective, there is one major problem in fabricating a flash memory device that can measure up to the demand of the latest technology. In conventional flash memory devices, the right thickness of insulator is paramount. If the thickness is too small, electrons can leak out leading to a loss of data. On the other hand, the need for a minimum thickness creates a problem with the 'write' voltage. If the thickness of the insulator is maintained at present levels, and the size of the device is reduced, the voltage intended for one cell may inadvertently affect a neighbouring cell. This could lead to data being stored at the wrong place. Researchers are therefore now experimenting with new materials and chip designs to get around the problem. One of the most studied ideas in recent times is the use of nano-crystal structures embedded in the insulator [8-24] as opposed to the conventional continuous floating gate as proposed by Kahng and Sze in 1967 [7].



Figure 3.15 A schematic cross section of a nanocrystal-based memory device.

Tiwari and co-workers [8] have described the charging and discharging of electrons in their silicon nanocrystal-based memory device. The size of the silicon nanocrystals was 5 nm and separated by 5 nm which gave a threshold voltage of 0.2- 0.4 V with read and write times less than 100's of nanosecond at operating voltages below 2.5 V. The nanocrystal-based memory device consists of a discontinuous layer of highly conductive material (metal or polysilicon) embedded in the insulator of the MIS structure as illustrated in figure 3.15. In this figure, the first insulator is thinner than the second insulator which allows electrons to tunnel from the semiconductor to the nanocrystal. The thickness of the second insulator must be sufficient to block the electrons from leaking from the nanocrystal to the metal gate. The first and second insulators are known as the tunnelling and gate insulators respectively.

The writing, storing and erasing mechanisms were graphically illustrated by Tiwari and co-workers [8], and the mechanism of electrons tunnelling through the first insulator and the retention of the electrons in the nanocrystal is clearly illustrated by Shi and co-workers [15]. One of the main advantages of the nanocrystal memory device is once the power is turned off; the data retention is highly effective due to the data storage elements, i.e. embedded nanocrystals, being well isolated.

3.4.3 Ferroelectric Material Memory Device

When the gate insulator of a MIS device is formed using a ferroelectric (FE) material, the threshold voltage is determined by the sign and magnitude of the polarisation in the FE. Application of appropriate voltages to the gate electrode can switch the direction of polarisation thus leading to hysteresis in both the C-V plot and the current-voltage characteristics. The use of FE materials for such a memory application is attracting much attention [25-47]. An example of an inorganic ferroelectric material is $Pb(Zr, Ti)O_3$ (PZT), whose unit cell is shown in figure 3.16.



Figure 3.16 Crystal structure of Pb(Zr, Ti)O₃ (adapted from [38]).

Polarization of the FE material has been shown to have a significant effect on the flat band voltage shift in the C-V curve similar to that discussed in section 3.4.1 [26-31]. Beside the hysteresis in the C-V curve, hysteresis was also observed in the I-V characteristic of a MISFET incorporating an FE layer [26, 33] and FE capacitor [32]. Not only inorganic FE materials have shown potential in the fabrication of a memory device. Some organic materials, either pure or incorporating inorganic FEs, have emerged as potential candidate materials in memory devices [32-41]. Lim and coworkers [35] demonstrated non-volatile memory action in the metal-ferroelectricinsulator-semiconductor based on ferroelectric polyvinylidene fluoride (PVDF) and
Grell and co-workers [41] have shown an all organic ferroelectric-like memory transistor. They graphically illustrated the charge distribution in the PVDF film under different conditions together with the energy diagram as shown in figure 3.17.



Figure 3.17 Changes in internal polarization field direction and distribution of charges within the ferroelectric layer (top) and energy diagram (bottom) under (a) forward bias (accumulation) and (b) reverse bias (inversion) (after [35]).

Under forward (positive) bias, an accumulation layer was induced at the n-Si surface by the joint action of the applied voltage and the polarization field in the PVDF. The presence of the polarisation field enhances the band bending in the silicon, enhancing the accumulation of electrons at the Si/SiO₂ interface. Consequently, a positive voltage shift occurs in the C-V curve, as seen in figure 3.18 (a). On the hand, when sufficient reverse bias is applied, the ferroelectric polarisation reverses, reinforcing the action of the applied voltage and increasing the concentration of carriers in the inversion layer. As a result, the C-V curve shifted to a more negative voltage (figure 3.18 (b)).



Figure 3.18 Typical C-V plot of the ferroelectric memory device.

Based on the principle outlined by Miller and McWhorter [47], FE materials should be the material of choice for non-volatile memory device fabrication. In practice, however, there are many obstacles which might hinder progress towards the commercialization of FE non-volatile memory device. One of the main problems is the difficulty of forming an electrically switchable FE thin film on a silicon substrate which has good interface properties and long retention times [29, 31].

Without external interferences such as interface states or bound charges, the concentration of the carriers on the ideal FE/semiconductor interface is controlled mainly by the superposition of the applied field and the polarisation of the FE domains. Therefore, the hysteresis loop in the I-V characteristics of the FE device is expected to be anticlockwise [45] as for the C-V plot in figure 3.18. For non-ideal FE devices, the presence of space charges arising from carrier trapping in the FE

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produce a competing mechanism which can reverse the direction of the hysteresis as described by Koo and co-workers [26] using the model in figure 3.19.



Figure 3.19 Schematic energy band diagram of the ferroelectric memory device under different bias condition: (a) accumulation, (b) carrier trapping at positive gate bias, (c) depletion, and (d) carriers trapping at a negative gate bias. Inset is an I-V plot showings clockwise hysteresis loop (after [26]).

Under positive bias, the combination of applied and polarisation fields produce a high field across the oxide layer leading to electron injection from the silicon accumulation layer into the FE where they are trapped (a). This reduces the oxide field, causing a field reversal (b) when the applied voltage is reduced. Thus the current flowing at this voltage on the reverse sweep will be lower than on the forward sweep. Under negative bias, the polarisation switches direction. Now the combination of applied and polarisation fields encourage the detrapping and transport of electrons back to the silicon (c), returning the system to its initial condition, following the path (c)-(d)-(a).

3.4.4 Polymer Memory Devices

3.4.4.1 Introduction

In recent years, semiconducting polymers have attracted much attention due to their application in optical and electronic devices. Interestingly, some of these polymers have exhibited switching and memory effects which have drawn a substantial number of researchers to investigate this particular area of technology [48-61]. Carchano and co-workers [48] first observed reproducible switching in Au-Polymer-Au junctions in 1971 by manipulating the glow-discharge polymerization technique to form a polymer thin film. The monomer used in their experiment was styrene and the resulting devices displayed a resistance ratio $>10^7$ and could be switched more than 2000 times. So long as the film thickness was less than 150 nm, the threshold voltage increased linearly with the film thickness. They suggested that the circular holes on the gold electrodes after each switching might have been due to current-carrying filaments. However, such an effect often accompanies electrical breakdown of weak spots accompanied by thermal evaporation of the localised region of the electrode.

Henisch and Smith [49] have also demonstrated a switching phenomenon in organic polymer films. Interestingly they fabricated organic switching devices from different types of polymer such as polymethylmethacrylate, polyethylmethacrylate and polystyrene using electrodes made from graphite, molybdenum and NESA glass. They were able to show that switching occurred in every device they fabricated. Henisch et al [50] elucidated the switching phenomenon in measurements on thin films of polymethylmethacrylate on molybdenum, silver, copper, graphite, Nesa and Nesatron substrates, using counter electrodes of pyrolytic graphite. They loosely envisaged that the trapping of electrons, injected from the metal electrode, caused a build-up of the electron potential at the metal/polymer interface. This electron potential prevented the net injection of further electrons (carriers) from the metal. The electron potential or trapped space charge distance was thought to be associated with the barrier (Schottky barrier) thickness formed at the metal/polymer interface.

Some groups [51-53] have shown that switching effects occur in conducting polymers such as polycrystalline Cu:7,7,8,8-tetracyanoquinodimethane (Cu:TCNQ). Potember and co-workers [51] first observed the switching effect in a lamellar structure with a film of microcrystalline Cu-TCNQ sandwiched between Cu and Al electrodes where the Cu-TCNQ was grown on the Cu substrate via a spontaneous electrolysis technique. They suggested that the bistable switching and memory effect in these thin films was a bulk phenomenon of the organic semiconducting material. Iwasa and co-workers [52] used a mixed-stack of tetrakis(methyltelluro) tetrathiafulvalene(TTeCTTF)-TCNQ to demonstrate a reproducible current switching effect in their device. Oyamada et al [53] co-deposited Al₂O₃ and polycrystalline Cu-TCNQ to produce their switching device which consisted of a uniform

charge transfer complex thin film. They suggested that a thin Al_2O_3 layer between the aluminium anode and Cu:TCNQ layers created the reproducible switching effect in their devices.

Gao et al [54] showed the electrical switching property in a vacuum deposited amorphous organic thin film of melamine cyanurate (MC). The MC layer performed as a semiconductor layer in forward bias. However when high applied forward bias was followed by application of reverse bias the MC layer behaved as a pure resistor. The switching from resistor to semiconductor states could only be achieved reproducibly if the negative scan took less than 100 s. In the same study, Gao et al [54] also inserted the MC layer between the ITO anode and a hole transport layer formed from N,N'-bis (3-methylphenyl)-N,N'-diphenyl-benzidine (TPD) to fabricate a voltage-controlled switchable organic electroluminescent (OEL) device. This OEL device again showed reproducible switching.

Bandyopadhyay and Pal [55] demonstrated that their device, fabricated by spin casting Rose Bengal onto an ITO-coated glass substrate and using aluminium as a top electrode exhibited a large electrical conductance switching with an ON:OFF ratio of 10^5 . The high ON-OFF ratio in Rose Bengal based devices was attributed to their low OFF-state leakage current. This device showed low conducting state (OFF-state) when the voltage was swept from positive voltage and a high conducting state (ON-state) when the voltage was swept from the opposite direction. They believed that this switching effect arose from the restoration of the conjugation chain in the molecule via electroreduction. Initially, without any donor group, the π -electron clouds were attracted toward the electron-withdrawing groups which surround the

Rose Bengal molecule. Consequently, the concentration of electrons in the π -electron clouds was decreased. This was deemed to be responsible for the disruption of the conjugation in the molecule so that it behaved as an insulator. Under a reverse bias that was above the reduction potential, the molecule received an electron and the conjugation was restored and the device was switched to the ON-state. On the other hand, under suitable forward bias, the molecule was oxidised by removing the extra electron added in the reverse bias and the device was switched to the OFF-state.

Majumdar et al [56] show that a device made by spin casting regioregular poly [3-(6methoxyhexyl) thiophene] (P6OMe) has the potential to be used in data-storage applications. They found that the charge stored in the polymer layer near the metal/polymer interface depended on the magnitude of the voltage applied across the device. Furthermore, they argued that the stored charge controlled the device current. Majumdar et al [57] further revealed that their devices have the capability to retain the stored charges for more than 2 hours and that the relaxation of the stored charges was sufficiently slow for memory applications.

Taylor and Mills [58] showed that diodes made by electropolymerisation of the low band gap polymer poly(4-dicyanomethylene-4H-cyclopenta[2,1-3,4-b']dithiophene) (PCDM), onto indium tin oxide (ITO) coated glass slides with aluminium as a top electrode exhibited a reversible bistability in the current-voltage (I-V) characteristics. The 'high' conductance state was observed when a positive bias was applied to the ITO electrode, while a 'low' conductance state was observed when the device was under negative bias. In their subsequent study of the effect, Mills and co-workers [59] suggested that the reversible bistability was related to a thin depletion region formed at the polymer/ITO interface (in which the space-charge is defined by a thin layer of ionized acceptors (BF_4)). Field-induced drift of these dopants to and from the electrode was thought to control charge injection and hence current through the device.

In summary, many studies have been undertaken of switching and memory effects in polymer semiconductors. The research in this particular area first emerged in 1971 [48] with much attention being given to the topic by researchers from different backgrounds. The main feature in most studies is the fact that the polymer itself can be manipulated as a switching or memory device. Therefore in chapter 5 we focus attention on elucidating the very promising switching characteristic in ITO/PCDM/Al diodes which was first observed by Mills and co-workers [59].

3.4.4.2 Polymer Floating Gate Memory Device

It has been argued that, the simple switching effect described in the previous section has limited practical application [60]. The success of inorganic flash memory devices incorporating either a continuous floating gate or a discontinuous nanocrystal layer as discussed in section 3.4.1 and 3.4.2 has triggered a new line of exciting research in polymer memory devices. By embedding a floating gate in-between two insulators, some authors have shown that polymer MIS devices have the potential to act as memory devices [61 - 67]. For example, Ma et al [61] describe an organic bistable device, with a trilayer structure consisting of organic/metal/organic layers sandwiched between two metal electrodes as shown in figure 3.17. The organic

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material used by Ma and co-workers [61] was 2-amino-4,5-imidazole-dicarbonitrile (AIDCN). When the device was biased above some critical voltage, the current switched through six orders of magnitude from a high-impedance state to a low-impedance state.



Figure 3.20 *Memory device structure (a) and energy diagram (b) (filled-circles are holes and empty-circles are electrons) as proposed by Ma and co-workers [61].*

Slow Al evaporation coupled with the introduction of a small amount of AIDCN resulted in the formation of metal nano-clusters (see figure 3.20) with an optimum volume ratio of Al:AIDCN = 3.3:1 [62]. The nano-clusters consist of a metallic Al core with AIDCN coatings. Under sufficient forward bias, free electrons in the metallic cores of the nanoclusters were able to tunnel through the barrier. As a result, the Al-nanocluster became polarised and the charges were stored at both sides of the middle layer as shown in figure 3.20 (b). Therefore the adjacent organic layers were able to undergo a conductance change (from OFF to ON) upon forward bias.

Furthermore, Ma and co-workers showed that the device displayed a non-volatile memory effect and the device remained in the low-impedance state even when the power was off. The high-impedance state could be recovered when the reverse voltage was applied. Based on their experimental data Ma et al [62], suggested that the bistability of the device was very sensitive to the nanostructure of the middle metal layer which was thought to consist of metal nanoclusters, separated by thin oxide layers, which behave as the charge storage element. In a further development, He and co-workers [63] electrically connected the middle metal-nanocluster to a predeposited Al strip to measure the potential of the nanocluster as well as acting as a third terminal for the I-V measurements.

At first, the memory device fabricated by Ma and co-workers seems to consist only of metal/organic/metal-nanocluster/organic/metal layers. However, a closer look reveals that they actually fabricated a memory stack with the metal nanocluster layer separated by a more resistive material which can be considered as an insulator. Practically, therefore, their device is similar to a floating gate memory device with metal nanoclusters embedded in the insulator. Some studies have directly employed nano-particles as a floating gate in a MIS memory device [64-67], with basic device operation similar to the inorganic floating gate memory device as discussed in sections 3.4.1 and 3.4.2. Developing easily processed memory devices is important for the development of polymer electronic circuits. Therefore, in addition to investigating the switching effect in PCDM diodes, the present study had the second aim of fabricating a polymer flash memory device.

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4.1 Introduction

Although the research described in this thesis investigated two different types of device, i.e. Schottky diode and MIS (flash) memories, nevertheless most of the analytical techniques were similar. However, the main device fabrication techniques were significantly different. Electrochemical polymerisation (electropolymerisation) was employed for the PCDM diode, while the conventional spin coating technique was employed for the flash memory and associated devices. All device fabrications were conducted in a class 10,000 clean room to minimise atmospheric contamination. In the following section we describe the main materials used including the preparation of the polymer solutions. This is followed by a description of the fabrication techniques themselves. Finally, the analytical techniques used for determining surface morphology, and for undertaking spectroscopic and electrical analyses are discussed.

4.2 Materials

In this study, the two main organic semiconductor materials used were poly (4dicyanomethylene-4H-cyclopenta [2, 1-b: 3, 4-b'] dithiophene (PCDM), and poly (3hexylthiophene-2, 5-diyl) (P3HT). PCDM was used to fabricate the Schottky diode memory device, while P3HT was used to fabricate the flash memory device. Polysilsesquioxane (PSQ) was used as an insulator in the flash memory device.

4.2.1 PCDM

CDM monomer was supplied as a dark metallic powder by Dr. P. J. Murphy, Dept. of Chemistry, University of Wales, Bangor. It was produced in a multi-step synthesis described by Jordan and co-workers in 1970 [1]. Full details of the synthesis have been provided by Mills [2] and will not be repeated in this section. As seen in figure 4.1, the monomer is a carbon-bridged dithiophene unit in which two electronwithdrawing cyano groups are connected to the thiophene units via a carbon bridge. The monomer was then polymerised electrochemically to produce the PCDM film following Ferraris and Lambert [3] and Mills and co-workers [4, 5].



Figure 4.1 Chemical structure of the CDM monomer showing two cyano moieties bridging two thiophene-based units.

CDM is insoluble in all common solvents and to our knowledge will only dissolve in nitrobenzene. Since CDM and nitrobenzene are electrically non-conductive, a supporting salt is needed to transport the electrons needed to initiate the electropolymerisation. The supporting salt also provides the dopant cations necessary for rendering the polymer conductive. The electrolyte solution, then, was a solution of the monomer (0.01 mol dm⁻³) and tetrabutylammonium tetrafluoroborate-TBATFB-(0.1 mol dm⁻³, Aldrich Chemical Co., UK). The solution was degassed by bubbling nitrogen through it for 20 minutes and either used immediately or stored in an airtight flask in the dark at 4°C to minimise photo-oxidation. When recovered from storage nitrogen was once again bubbled through the solution in the electrochemical cell prior to use.

4.2.2 P3HT

P3HT was chosen as the organic semiconductor for the second part of this study because the characteristics of this material have been well documented [6-14]. The P3HT solution for spin coating was prepared by weighing 0.0752 grams of regioregular poly(3-hexylthiophene-2,5-diyl), Sigma-Aldrich, into a 5 mL volumetric flask, then topping up with chloroform (Aldrich Chemical, UK) producing a 1.50 mmol dm⁻³ polymer solution. The solubility of the P3HT in chloroform was enhanced by placing the volumetric flask in a warm ultrasonic bath at a temperature of around 50°C and sonicating for 30 minutes to 1 hour. When no solid was visible the solution was filtered by syringing through a Millipore Millex-FG Hydrophobic PTFE 0.2 μ m filter. The P3HT was then stored in an airtight bottle in the dark at 4°C.

4.2.3 Polysilsesquioxane

Polysilsesquioxane (PSQ) is a general term given to a new family of hybrid organicinorganic composites with a wide range of desirable physical and chemical properties inherited from the inorganic and organic materials respectively. PSQ is represented by the empirical formula $RSiO_{3/2}$, where R denotes the organic functional group in the main chain. R can be any derivative ranging from a simple hydrogen atom in poly (hydrogen silsesquioxane) to a more complex hydrocarbon group such as the combination of methyl-phenyl (CH₃-(C₆H₅)) as in poly (methylphenyl silsesquioxane). Additionally, in PSQ each silicon atom is bound to 3/2 (sesqui) oxygen atoms.

Before any thermal curing process is performed, the molecular structure of the PSQ material typically consists of a cage structure (see figure 4.2 (a)). During thermal curing, part of the cage structure collapses and forms a ladder-like structure (see figure 4.2 (b)). Upon further thermal curing, some of the cage structure totally collapses and forms a network structure such as that depicted in figure 4.2 (c). In this example, however, the R group is replaced by both CH₃ and NCO.



Figure 4.2 Chemical structure of polysilsesquioxane in (a) cage structure, (b) ladder-like structure, and (c) network structure (after [15, 16]).

PSQ materials have been recognised as potential candidates for low dielectric constant materials [17] and have the advantage of being soluble in a wide variety of organic solvents which enhance their processability. PSQs have found applications in industry since they were first synthesised by Scott in 1946 [18]. Examples that can be found in the literature include thin film transistors (TFT) [19], porous ceramic films [20], low-k dielectric constant coating agent [21] and nonlinear optical response applications [22].

For flash memory applications, the PSQ layer adjacent to the semiconductor should be thin to encourage electron tunnelling. However, preliminary studies showed that if the film was too thin (<200 nm) the density of pinholes becomes too high and the quality of the final device was poor. On the other hand, if the PSQ film was too thick (>400 nm), the quality of the PSQ surface was badly affected. This may be due to the viscosity of the PSQ solution being too high so that air bubbles formed inside the film during the early stage of the thermal curing process. To minimise such problems, the optimum film thickness found to be ~280 nm. Hence, a 5% solution of PSQ was prepared by dissolving 0.4226 grams of poly(phenylmethylsilesquioxane) flake, 90% phenyl, 10% methyl (Gelest Inc.), in 10 mL of methyl ethyl ketone (2-butanone) (Aldrich Chemical, UK). After all the flake was dissolved, the solution was filtered by syringing through a Millipore Millex-FG Hydrophobic PTFE 0.2 μ m filter. The solution was stored in the dark in a refrigerator below 5°C.

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4.3 Substrate preparation

The main substrate used in this study was indium-tin-oxide (ITO)-coated glass. In the earlier part of the study, i.e. during PCDM diode fabrication, the ITO-coated glass (20 Ω /square) was purchased from Pilkington, UK and was supplied in squares 350 mm x 350 mm in size. For the second part of the study, i.e. the fabrication of all devices which led to the flash memory device, ITO-coated glass (~10 Ω /square) was purchased from Sigma-Aldrich Chemie GmbH, Germany and was supplied in pieces with the same dimensions as a microscope slide (75 mm x 25 mm). The as-supplied substrates were cut into smaller pieces, 37.5 mm x 25 mm for the first study and 25 mm x 25 mm for the second study.

The cleanliness of the substrate is very important to ensure the smoothness of the deposited film. This turned out to be critical in the flash memory work where electrode defects could affect the integrity of the insulating layer. In this case the simpler cleaning protocol used for the PCDM diodes was significantly enhanced. Prior to electrodeposition of the PCDM the substrates were cut to the appropriate size and first washed with cold water. Then Decon 90[®] (Scientific Services Ltd, UK), a bleach replacement, was rubbed onto the surface with a cotton bud. From this moment onward, touching any surface of the substrate should be avoided to reduce possible contamination of the substrate prior to film deposition. Hence, the substrate was placed in a special sample holder to avoid direct contact. The substrate was then washed with cold water for about one minute followed by hot water for another one minute and this procedure repeated five times. After that, the substrate was rinsed

with running ultra-pure water (Millipore Q system) for about five minutes. Finally, the substrates were blow-dried with hot air before placing in the electrochemical cell.

For the second part of the study, it was necessary to eliminate any hydrophilic mark on the surface because of the hydrophobic nature of the PSQ solution. Any such marks led to poor adhesion of the PSQ on those areas and subsequently to pinhole formation. To minimise these problems the following cleaning procedure was adopted. Firstly, the ITO-coated glass was cut to the appropriate size and Decon 90[®] was applied thoroughly on all surfaces using a cotton bud. The ITO-coated glass was then placed inside a sample holder filled with Decon[®]90 solution and sonicated for about 10 minutes. Next, the substrate was thoroughly washed in hot water to remove all the detergent. This was followed by a thorough rinsing in ultrapure water for at least 1 minute. Without touching any surface of the substrate, it was then blown dry using a high pressure compressed air jet to remove all water marks immediately. Lastly, the substrate was blown dry using hot air to remove any remaining traces of moisture.

Following this first wash, the substrate was put back into the sample holder, this time filled with acetone, and sonicated for another 10 minutes. The drying process was then repeated as described above. After that, the cleanliness of the substrate was examined using an optical microscope (Nikon Eclipse ME 600). Further cleaning might be needed if any contaminants remained on the substrate. However, further cleaning only involved the simple process of gently rubbing the substrate surface with Decon 90[®] using the cotton bud and then immediately washing and drying the substrate. The clean substrate surface was then made hydrophobic by soaking it with

any hydrophobic solvent such as acetone or iso-propanol. Finally, the cleanliness of all the substrates was confirmed under an optical microscope prior to film deposition.

4.4 Film Deposition

In this study, we employed two main methods of depositing the polymer films. In the first part of the study an electrochemical deposition was employed to fabricate a PCDM film. On the other hand, films of PSQ and P3HT were prepared by the more simple and straightforward spin-coating technique.

4.4.1 Electropolymerisation of PCDM Film

The CDM monomer solution and the ITO-coated glass substrate were prepared following the method described in section 4.1.1 and 4.2 respectively. Prior to the deposition of the PCDM film, the CDM monomer solution was taken out from the refrigerator and degassed with nitrogen for at least 20 minutes to dissolve any coagulants or sediments that may have been created during storage. The degassing of CDM monomer solution was the also performed in between each electropolymerisation cycle as well as before storing any residual solution. The electropolymerisation of the CDM monomer was conducted in a three electrode cell controlled using a Princeton Applied Research EG&G model 273 potentiostat/galvanostat connected to a differential electrometer module model 273.

Figure 4.3 illustrates the apparatus used in this study. The cell consisted of a 50 mL beaker containing monomer solution into which the electrodes were dipped to a depth of approximately 3 cm. Prior to use, the beaker was washed with ultrapure water and acetone then dried in an oven. The electrodes were suspended in the solution using a PTFE cap to the beaker, which housed a copper contact for the working electrode and openings for the reference and secondary electrodes. The working electrode consisted of the ITO-coated glass. The reference electrode consisted of a length of clean silver wire (99.9% 0.5 mm diameter, Advent Chemicals, UK). Silver wire is not recognised as a standard electrode but it was used in this work for convenience. As long as it was cleaned prior to use it can be considered to be a reproducible "quasi-reference" electrode. The secondary electrode was platinum foil (dimension 7 mm x 6 mm).



Figure 4.3 Illustration of the apparatus used for the electrodeposition of the PCDM films.

The polymerisation followed the procedure reported by Roncali and co-workers [23] and modified by Taylor and co-workers [24] and consisted of three steps controlled by the potentiostat. Firstly, a nucleation step was performed using a slightly higher potential than the growing step to create a high density of nucleation sites on the substrate. The potential was then stepped down to the growing potential where polymerisation occurred over a period of time. The potential was then stepped down to 0V to dedope the polymer. This step generally required the dedoping current to fall below 0.02 mA and then to continue dedoping for a fixed period of time. A typical growing cycle for PCDM is given in table 4.1.

Polymerisation Condition	Value
Nucleation potential (V)	2
Nucleation time (s)	10
Step potential (mV/s)	50
Growing potential (V)	1.8
Growing time (s)	600
Step potential (mV/s)	50
Dedoping potential (V)	0
Dedoping time upon reaching 0.02 mA (s)	300

Table 4.1: Typical electropolymerisation cycle for	or PCDM
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After polymerisation, the sample was removed from the monomer solution and rinsed with acetone for 10-15 seconds to remove excess monomer and solvent and then dried under a stream of nitrogen. The sample was then immediately removed and stored in the dark under vacuum before spectroscopic analysis. This procedure was repeated for several more cycles of electropolymerisation using the same monomer solution.

4.4.2 PSQ and P3HT Films Deposition

Films of both PSQ and P3HT were prepared by spin coating using an Electronic Microsystems Ltd Model 4000 Photoresist Spinner. For both materials, a Volac disposable glass pipette was used to introduce the PSQ or P3HT solution onto the substrate and the spinner rotated at a speed of 1000 rpm for 60 seconds.

Immediately after spin-coating, the PSQ film was transferred into the nitrogen filled Carbolite oven for the thermal curing process. The oven can be programmed to increase the temperature automatically at a specific rate until the target temperature is reached. In this study, the curing process was performed by slowly increasing the temperature at the rate of 4°C per minute until the temperature reached the first target temperature of 70°C. The temperature was maintained at 70°C for 60 minutes to drive off the solvent and then increased at the same rate to the second target temperature of 200°C. The temperature was then maintained at 200°C for 120 minutes before it was increased to the final target temperature of 350°C which was maintained for another 60 minutes. Finally the oven was cooled down to room temperature over ~10 hours to reach room temperature. The usual practice was to allow the sample to cool down in the oven overnight. All the curing and cooling processes were performed in an inert environment, by introducing 0.5 psi of nitrogen flow into the oven before the curing process started. The nitrogen flow was maintained throughout the curing and cooling processes. The quality of the PSQ film was first observed under an optical microscope to make sure that there were no pin holes or obvious contamination in or on the film. Prior to any further steps, the PSQ film was kept under vacuum to reduce any possible contamination by extraneous particles from the environment. Depending on the desired device configuration, the PSQ film underwent further device fabrication steps.

After spin-coating the P3HT film (either onto the ITO-coated glass or onto the PSQ film), the samples were immediately placed under vacuum and heated at 70°C for 1 hour in the Büchi Glass Oven B-50. In order to avoid any light-induced reaction (such as photo-oxidation) in the P3HT film, the oven was covered with aluminium foil. The oven was evacuated using a DIVAC 0.6 mini-pump system. Prior to deposition of P3HT onto a PSQ-coated substrate, the PSQ film was first treated with hexamethyldisilazane (HMDS) to enhance semiconductor adhesion. HMDS reacts with the PSQ surface in a process known as Silylation forming a strong bond to the surface and rendering it hydrophobic, thus enhancing the semiconductor adhesion. Several different approaches have been employed to treat the insulator surface with HMDS [25, 26]. In this study, a few drops of HMDS were placed on the PSQ film (the entire PSQ surface was covered) and left for approximately 10 seconds on the spinner. Then the substrate was spun at 1000 rpm for 60 seconds, after which the chosen semiconductor was spun on. Prior to any further device fabrication procedures or analysis, the film sample was kept in the dark under vacuum.

4.5 Metal Evaporation

In this study, all the devices were completed by furnishing with a metal counterelectrode thus forming a simple diode or MIS structure. In the case of the flash memory device, a thin layer of evaporated metal was deposited between two insulator (PSQ) films. The bottom electrode for all the devices was ITO-coated glass, while the top (counter) electrode was either aluminium or gold. The aluminium counter-electrode was evaporated through a shadow mask onto the film at a pressure of $\sim 10^{-6}$ torr using a turbo pumped system (Balzers Evaporator Type: TSF 012, Nr: PM Z01 105, 42VDC). The gold electrode was deposited through a shadow mask onto the film at a pressure of $\sim 10^{-8}$ torr using Edwards Auto 306 Turbo Evaporation System. After that, all devices were kept under vacuum in the dark prior to any electrical characterisation.

4.6 Device Customization

The PCDM memory device was prepared by sandwiching a single layer of PCDM film between two metals while the flash memory device involved sandwiching the memory stack-PSQ/Au/PSQ/P3HT-between two electrodes. All film preparation and metal evaporation techniques were as discussed in the previous section and in this section different device structures will be briefly illustrated.

4.6.1 PCDM Memory Diode

The PCDM diode structure is illustrated in figure 4.4 and the top electrodes were deposited through a circular shadow mask 1.8 mm in diameter. For the purpose of undertaking capacitance-voltage measurements, a PCDM MIS diode was also fabricated by spin coating $\sim 0.5 \mu m$ of photoresist (S1818) onto a newly prepared PCDM film. All the MIS devices were cured at 114°C for 2 minutes and immediately thereafter were stored under vacuum overnight prior to the aluminium top electrode deposition.



Figure 4.4 Schematic diagram of (a) a Schottky diode and (b) a MIS diode based on the semiconductor PCDM.

4.6.2 Polymer Flash Memory Device

In order to understand the behaviour of the flash memory device a number of precursor devices were fabricated and examined. The structure of these devices is shown in figure 4.5. The top electrodes were deposited through a circular shadow mask with a diameter of 3.5 mm for devices (a) and (b), and 1.8 mm for devices (c) and (d).

4.6.2 (a) ITO/P3HT/Al Schottky Diode

The ITO/P3HT/Al structure allowed the Al/P3HT Schottky contact to be examined from which information such as the current-voltage characteristic, depletion width and doping density could be obtained.

4.6.2 (b) ITO/PSQ/Au

The ITO/PSQ/Au MIM structure allowed the insulating quality of the PSQ insulator to be determined.



Figure 4.5 Schematic diagram illustrates the precursor devices ((a) - (c)) and polymer flash memory device (d).

4.6.2 (c) ITO/PSQ/P3HT/Al

The device in figure 4.5 (c) is the MIS capacitor structure on which the flash memory device is based. This structure should confirm the integrity of the PSQ layer after exposure to the P3HT solution during spin coating. It is an unusual structure in that the aluminium electrode forms a Schottky contact to the P3HT. Thus irrespective of bias polarity a depletion region exists at the PSQ or the aluminium interfaces with the P3HT. This affords a degree of current limitation which protects the device, and in particular the PSQ layer from voltage overstress.

4.6.2 (d) The Flash Memory Device

Device (d) in figure 4.5 shows the structure of the flash memory fabricated in this study. The only difference from the MIS capacitor (figure 4.5 (c)) is that the PSQ film is grown in two steps/ between which a thin gold film (~20 nm) is evaporated onto the first PSQ film.

4.7 Device Characterisation

This section describes the various spectroscopic, microscopic and electrical techniques used to characterise the materials employed and the devices fabricated in this study.

4.7.1 Spectroscopic Analysis

Spectroscopy is a powerful tool for studying the chemical characteristics of organic materials, thus providing vital information needed when discussing device behaviour. In this study, both ultra-violet/visible (UV/Vis) and Fourier Transform Infrared (FTIR) spectroscopy were used to identify the reason for the major differences in the electrical behaviour of the PCDM diodes.

4.7.1.1 Ultra-violet/Visible spectroscopy

A Hitachi model U-2000 double beam, ultra-violet/visible (UV/VIS) spectrophotometer was used for UV/VIS analysis of polymer samples. This apparatus consisted of a deuterium discharge lamp for UV light emission, with an automatic switch-over adjustable within the range 325 to 370 nm. The primary beam was passed through a half-silvered mirror beam splitter, which transmitted approximately 50% of the light to produce a sample beam, and 50% reflected light to form a reference beam. Silicon photodiode detectors were used for detection of the transmitted and reflected beams over a wavelength range from 190 to 1100 nm. The sample chamber remained light-tight during the analysis to avoid contamination of the sample spectrum by extraneous light sources.

4.7.1.2 Fourier Transform Infra-Red spectroscopy

Infrared analysis was undertaken using a Bomem Michelson MB-100 Fourier transform infra-red (FTIR) spectrometer incorporating a P/N 19650 series monolayer/grazing angle accessory (Graseby Easy Ltd., UK). The spectrometer used Win-Bomem Easy (version 3.04, level II) software to control a double pendulum-design interferometer with potassium bromide corner cube mirrors. The excitation laser was a red emitting (633 nm) helium/neon laser, producing a spectral precision of 0.01 cm⁻¹, and the emitted light was detected using a deuterated triglycine sulphate pyroelectric detector giving a spectral range of 6000 to 350 cm⁻¹. The sample was placed onto the spectrometer stage within the grazing angle accessory and the spectrum recorded at different grazing angles between 70° and 80° to produce the most intense spectrum. Spectra were normally recorded between 500 and 4000 cm⁻¹ where all of the sample spectral peaks were positioned.

4.7.2 Surface potential measurement

Following preliminary electrical measurements, the possibility arose that ionic movement could account for some of the effects observed. Therefore, surface potential measurements were made in an effort to detect the possible movement of ionic charges in the PCDM film. All the surface potential readings were taken by using a TREK electrostatic voltmeter, model 320B surface potential probe (Kelvin Probe). In order to gain access to the top surface of the stressed PCDM film, voltages
were applied to the film via a removable, circular aluminium disc of diameter 10 mm. The experimental set up is shown in figure 4.9.

The initial surface potential was taken before the Al disc was placed on top of the film. By referencing this reading to that from the bare ITO surface, the contact potential difference, V_{cpd} , between ITO and PCDM can be determined. Assuming that that work function of ITO , $\phi_{ITO} = 4.8eV$, we may then determine that of PCDM, ϕ_{PCDM} , i.e.,

$$qV_{cpd} = \phi_{PCDM} - \phi_{ITO}. \tag{4.1}$$

If, on scanning from ITO to PCDM, the step change in potential is negative, this would be consistent with the formation of a Schottky barrier at the ITO/PCDM interface.



Figure 4.6 Experimental set up to apply the voltages before surface potential reading was made.

Following the initial measurement the Al disc was placed carefully on top of the film for 30 minutes and the reading taken within the first few seconds of removing the disc. Following this reading, the disc was replaced and a bias applied to the device via the Al disc (positive or negative bias) overnight. A further surface potential reading was then taken the following morning after removing the Al disc. The position of the measurement was kept constant (the same position for every different voltage) using an x-y stage with an electronically controlled movement.

4.7.3 Atomic Force Microscopy

In this study, the atomic force microscope (AFM) was employed to determine the thickness of the various films prepared as well as their surface roughness. The AFM equipment consisted of a Digital Instruments Nanoscope 3A Multimode Scanning Probe Microscope (SPM) with controlling electronics, an interfaced personal computer and two monitors which were used to display control settings and the captured image. The SPM unit comprised a lead zirconium titanate (PZT) piezoelectric scanner, an imaging laser, the probe holder and sample support and a position sensitive, quadrant photodiode detector. The maximum scan size possible with the PZT scanner was 200 μ m by 200 μ m with a maximum vertical range of 8 μ m. Samples of PSQ and P3HT films on ITO substrates were cut to fit into the sample holder and then fixed onto the 15 mm diameter steel circular disks using adhesive tabs. A very thin line was drawn across the polymer film by using a thin sharp blade. The disk was then placed onto the magnetic sample holder within the SPM. One of a variety of cantilevered probes incorporating a pyramidal tip which

included silicon nitride and crystal silicon probes was chosen depending on the desired analysis method.

There are a number of imaging methods available using AFM, namely contact mode, non-contact mode and tapping mode. Contact and non-contact mode employ the cantilever as a spring which permits the tip to move in response to the different surface forces near to the film molecules. Any shift in the position of the cantilever is recorded by the detector. Repulsive forces between the tip and the sample atoms are employed to image the surface when the AFM is in contact mode. The analysis of soft, deformable samples is normally done in the non-contact mode. In this mode the tip is held further away from the sample where the attractive and repulsive forces are weaker. In the tapping mode, the cantilever is vibrated at its resonant frequency and the tip brought close to the surface, where it makes intermittent contact (taps) which causes the oscillation amplitude to decrease. In this study the tapping mode was selected to measure the thickness of the polymer film (PSQ and PCDM) as this mode minimised the damage caused by the lateral forces exerted in contact mode. The tip was scanned across the line drawn earlier using a sharp blade. An electronic feedback loop to control the position of the tip with respect to the sample surface was utilised as a control mechanism for precise tip-sample interaction. The off-line Nanoscope version 4.1, software was employed to enhance and analyse the raw image.

4.7.4 Electrical characterisation

All the electrical characterisations were performed under a high vacuum in a dark steel chamber. Both the DC and AC characterisation equipment were controlled using Visual Basic software programs. Figure 4.11 illustrates the sample holder and vacuum chamber used for the electrical characterisation.



Figure 4.11: The vacuum chamber and sample holder used for electrical characterisation of the diodes. The parts coupled with numbers 1 to 5 are the lead connections to the external equipment. 1 is connected to the temperature controller, 2 to the power supply, and 3, 4, and 5 are connected to the measurement bridge with 3 and 4 the connections from the top electrode and 5 the connection from the gate electrode.

The chamber was evacuated with a rotary pump backing a silicone oil diffusion pump. At any time, two top electrodes and a gate electrode were connected to leads in the connector block by 0.025 mm diameter of 99.996% pure gold wire (Advent Research Materials Ltd) bonded to the electrodes with conductive silver paint. The second top electrode was connected as a spare device in case of damage to the first device. The temperature of the sample holder was controlled by a Eurotherm 91e temperature controller employing a chromel-alumel thermocouple. The sample was heated using two electrical heating resistors and cooled down using a copper heat sink immersed in liquid nitrogen. The two electrical heating resistors were connected to a power supply, Farnell E30-28, 30V, 20A DC.

4.7.4.1 DC characterisation

Since our devices were simple diodes, the DC characterisation simply involved applying a voltage to the gate (bottom) electrode and measuring the current output through the top electrode.

4.7.4.1 (a) PCDM diode

DC characterisation of the PCDM diode was conducted using a Hewlett Packard 4140B pA meter/DC voltage source which was capable of applying negative and positive voltages in the range -10V to +10V to the device and measuring currents in the range 1 pA to 1 mA. The voltage source was allowed to stabilise for at least 30 minutes prior to the DC measurement and after each step change in voltage, device currents were allowed to stabilise for 60 seconds. DC measurements were started

after the pressure in the chamber had reached 10⁻⁵ torr. Common measurement parameters for the PCDM diode are shown in table 4.2. The positive voltage sweep indicated here was followed immediately by a sweep in the reverse direction. The AC measurements were only conducted after voltage sweeps in both directions were completed.

Measurement parameters	Value
Start voltage (V)	-5
Stop voltage (V)	+5
Step voltage (V)	0.02
Step delay time (s)	60
Step delay time (s)	60

 Table 4.2 Common DC measurement parameters for the PCDM diode.

4.7.4.1 (b) Flash memory devices

The DC characterisation of the flash memory devices in the second part of the study was conducted using a Keithley 617 Programmable Electrometer voltage source which can apply voltages in the range -40 V to 40 V to the device and measured currents in the range 1 pA to 1 mA. DC measurements were started after the pressure in the sample chamber had reached 10⁻⁷ torr. Common measurement parameters for the flash memory and precursor devices are shown in table 4.3. The positive voltage sweep indicated here was followed immediately by a sweep in the reverse direction. After voltage sweeps in both directions were done then the AC measurements were carried out.

Table 4.3 Measurement setting	s for the	e DC characterisatio	n for	flash	memory	and
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Measurement settings	Schottky Diode	MIM	MIS	Flash Memory
Start voltage (V)	-3	-40	-20	-20
Stop voltage (V)	3	40	20	20
Step voltage (V)	0.05	0.5	0.5	0.5
Delay time (S)	10	10	10	10
Hold time (S)	10	10	10	10

precursor devices.

4.7.4.2 AC characterisation

For AC electrical characterisation, an Agilent 4284A 20Hz – 1MHz Precision LCR meter was used. The capacitance and loss were measured as a function of frequency from 20 Hz to 1 MHz at a fixed voltage using a test signal of 50 mV. All AC measurements were conducted at room temperature except for an MIM device, where the measurement was performed in 10°C temperature increments from room temperature up to 130°C. Capacitance-voltage measurements were also carried out at fixed frequencies within the range 20 Hz to 1 MHz and the voltage ranges for the different devices as shown in table 4.4. The positive voltage sweep indicated here was followed immediately by a sweep in the reverse direction. The capacitance-voltage measurement was excluded for the MIM device because the capacitance and loss were independent of the applied voltage.

Measurement Setting	PCDM MIS Diode	Polymer Flash Memory Devices			
		Diode	MIS	Flash Memory	
Start voltage (V)	-10	-2	-20	-20	
Stop voltage (V)	10	2	20	20	
Step voltage (V)	0.2	0.05	0.5	0.5	
Delay time (S)	60	10	10	10	
Hold time (S)	60	10	10	10	

 Table 4.4 Setting for the capacitance-voltage measurement

4.8 References:

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5.1 Introduction

As mentioned in Chapter 1, this part of the study continues the earlier study by Mills and co-workers [1, 2] and further background details can be obtained from the work by Mills [3]. In this section, we start with an AFM analysis to determine the film thickness as well as the surface roughness. After that, the result from the currentvoltage characterisation is presented to show the memory effect and the lack of rectification in the PCDM diode. Current-voltage characteristics of PCDM produced subsequently from the same monomer solution are also presented showing the disappearance of the memory effect in the later device. Capacitance and loss versus frequency measurements were made to investigate the presence or otherwise of a depletion layer at the polymer/electrode interface. Surface potential measurements are presented to establish the contact potential difference between Al/PCDM and ITO/PCDM interfaces. This was then followed by the capacitance-voltage characterisation of the PCDM MIS capacitor to support our conclusion that a depletion region was present at both interfaces. Subsequently, the focus of the discussion shifts to the results of the spectroscopy analysis. This analysis was important since it gave information on the chemical structure of PCDM. In particular, we were interested in the presence of dopants in the polymer (FTIR) and determining the band gap (UV-Vis spectrum). In the discussion section, we followed changes in the PCDM properties from one batch to another so as to correlate the spectroscopy data with changes in the current-voltage characteristic of different PCDM diodes. It is noted that all the voltages in this part were applied to the ITO electrode.

5.2 Film Morphology

Figure 5.1 (a) is an AFM micrograph showing the morphology of the PCDM surface. The image shows a $5\mu m \ge 5\mu m$ region taken from a $10\mu m \ge 10\mu m$ scan. The root mean square (rms) surface roughness of the film was typically ~24 nm when measured over a $10\mu m \ge 10\mu m$ area and comparable therefore to the early studies by Mills and co-workers [2]. They found that the rms roughness of their film over an area $2\mu m \ge 2\mu m$ was 8.3 nm but this increased to 13.3 nm when the scanned area was increased to $5\mu m \ge 5\mu m$. These values are relatively low when compared with the sample thickness which can be measured from a cut edge of the film as shown in figure 5.1 (b).



Figure 5.1 *AFM images of typical PCDM film used for determining (a) roughness, and (b) film thickness.*

Typical PCDM film thickness from this study was estimated to be 253 nm (with film thickness ranges from 200 nm to 300 nm). Thus the overall roughness is less than 10% of the nominal film thickness. Using N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-bipenyl1-4,4'-diamine (α -NPD) as an active material, Koch and co-workers [4] showed that the rms roughness of the surface of their electrodeposited polymer was about 7% and had insignificant effect on the current-voltage characteristic of their devices. Therefore with this result in mind, we believe that the surface roughness is reasonable and should not have any significant effect on the current-voltage characteristic of PCDM.

5.3 Current-Voltage Characteristics

Since the work functions of aluminium and thiophene-based polymer films are normally significantly different, strong rectification was expected in the currentvoltage characteristic of the Al/PCDM/ITO device. In an earlier study, Taylor and Gomes [5] observed that an aluminium electrode showed a significant rectifying property with the thiophene-based polymer, poly(3-methylthiophene). However, figure 5.2 clearly shows that the semilog plot of current vs voltage is almost symmetrical, displaying an almost linear relationship for both polarities of applied voltage. This suggests an exponential rather than ohmic behaviour coupled with insignificant rectification. Interestingly, though, the current at low voltages was found to depend on the direction of the voltage sweep. For example, in figure 5.3 the device is in a 'high' conductance state when swept from 5V to -5V but in a 'low' conductance state when swept from -5V to 5V.



Figure 5.2 *Current-voltage characteristics of PCDM diode when the voltage applied* to the ITO electrode was swept from -5V to +5V.

In the present work the voltage sweep rate was 0.33 mV/s and therefore significantly lower than the 0.83 mV/s employed by Mills et al [1, 2]. Consequently, it was not necessary here to correct for the corresponding displacement current since it is negligible as evidenced by the inset plot in figure 5.3. The data from figure 5.3 is replotted on a log-log scale in figure 5.4. When scanning from positive to negative voltages, the plots for both polarities are similar, displaying ohmic behaviour in the range |V| < 1 V, but superlinear outside this range. In the reverse sweep, however, the current falls superlinearly through the negative voltage range yielding a current that is more than one order of magnitude lower at -0.1 V than at +0.1 V. When this scan is continued into the positive voltage range, the current, while increasing ohmically, nevertheless remains ~ one order of magnitude lower than for the initial sweep. However, above ~2 V, the current rises rapidly towards the initial values observed at 5 V.

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Figure 5.3 Log current-voltage characteristics of the PCDM diode for different voltage sweep directions. Inset is the linear plot showing that both curves pass through the origin.



Figure 5.4 Log-log plots of the current-voltage characteristics from figure 5.3.

The results presented in figures 5.2 to 5.4 apply to the device fabricated in the first cycle of a fresh monomer solution and corroborate the results obtained by Mills et al [1, 2]. In an effort to understand why the memory effect proved difficult to reproduce the characteristics were obtained for devices formed in successive cycles from the same solution. These are shown in the double log plots in figure 5.5, where PCDM 1 represented polymerisation cycle number 1 and PCDM 2 is for number 2 and so on.



Figure 5.5 Log-log plot of current vs voltage for PCDM diodes prepared in different cycles. (Δ) represents 5V to 0V, (\blacktriangle) 0V to -5V, (\bullet) -5V to 0V and (\circ) 0V to 5V.

The main changes observed in films grown in successive growth cycles are (a) a reduction in the magnitude of the memory effect and (b) a general decrease in the observed currents.

5.4 AC characteristics

The admittance of devices prepared sequentially from the same solution is shown in figure 5.6 to 5.8.



Figure 5.6 Capacitance versus frequency plot of Al/PCDM/ITO diode produced at different cycle from the same solution.

The general features of all the plots are similar and reflect the presence of a depletion region at one of the electrodes. Thus from the equivalent circuit in figure 3.4, the low-frequency capacitance in figure 5.6 can be associated with the depletion region.

At high frequency the capacitance represents the geometric capacitance of the device. From the plots in figure 5.6 to 5.8 one general trend can be identified; the frequency of the dispersion moves to lower frequencies for the film prepared at the later cycles.



Figure 5.7 Loss versus frequency plot of Al/PCDM/ITO diode produced at different cycle from the same solution.

Figure 5.8 shows the Cole-Cole plot of devices fabricated in this study. In this figure, the curves for PCDM 1, PCDM 2 and PCDM 3 clearly extended to a higher capacitance at low frequencies whereas for PCDM 4, the dispersion moved to a very low frequency (out of measurement range). The extension of the dispersion in PCDM 1, PCDM 2 and PCDM 3 may be explained by leakage through the depletion region, dispersive transport in the bulk or perhaps by the presence of Warburg impedance due to the presence of the impurities. Finally, as seen in figure 5.8 (inset),

the geometric capacitance of PCDM 3 and 4 is significantly higher compared to the other films suggesting a thinner film.



Figure 5.8 The data presented in figure 5.11 and 5.12 replotted in the complex admittance plane (Cole – Cole plot). Inset is the magnified section of the graph at high frequencies.

The extension of the arc for PCDM 1, 2 and 3 suggests that PCDM diodes have a distribution of relaxation time rather than single relaxation time. This is not surprising, since disordered organic materials are more likely to exhibit dispersive transport in the bulk region as shown in P3HT [6]. From figure 5.8, the value of the distribution factor for relaxation times, α , for each device was also estimated and tabulated in table 5.1. As seen from table 5.1, the value of α for PCDM 1 is much smaller than for PCDM 2 and 3 which suggest that PCDM 1 has a narrower

distribution and is close to single relaxation time. (When α is zero, the relaxation reduces to the Debye relaxation case with one time constant (τ_R)).

Device	Distribution Relaxation Time (α)
	(rad)
PCDM 1	0.12
PCDM 2	0.21
PCDM 3	0.27

 Table 5.1 Distribution factor for relaxation times of PCDM diode.

Although the Cole-Cole plot in figure 5.8 shows depressed curves, nevertheless the individual components in the equivalent circuit in figure 3.4 might still be estimated. In figure 5.8, the high frequency dispersion of PCDM 1 and 2 were asymptotes to the horizontal axis at ~153 pF, while the high frequency dispersion of PCDM 3 and 4 were asymptotes to the horizontal axis at ~400 pF, which corresponds to the series sum of the depletion layer capacitance, C_d , and the bulk capacitance, C_b , of the device. The depletion region capacitance, C_d , can be estimated by extrapolating the low frequency data to the horizontal axis, which gives approximately 12 nF for PCDM 1. Therefore, with a PCDM film thickness of 253 nm (see section 5.3), $C_b = 155$ pF and the top electrode diameter of 1.8 mm, the PCDM relative permittivity is estimated to be ~3.9, assuming that PCDM 1 contained less impurities than the other films. On the other hand, for PCDM 2 and 3 the arc is extended to higher capacitance. The low frequency capacitance for PCDM 2 and 3 were estimated from figure 5.8 by drawing the best arc through the curves which gives 17 nF and 19 nF respectively. Therefore the depletion region widths for PCDM 1, 2 and 3 were

calculated to be 7.3 nm, 5.2 nm and 4.3 nm respectively, suggesting the charge density in PCDM 3 was higher than PCDM 1 and 2. Finally, from the high frequency dispersion (~400 pF) and depletion region capacitance (19 nF) of PCDM 3 in figure 5.8, the film thickness of PCDM 3 was estimated to be ~ 240 nm.

5.5 Surface Potential and Fermi Level of the PCDM Film

Since the PCDM film was electropolymerised on top of the ITO-coated glass, the surface potential measurement was conducted to determine the contact potential difference between the grounded ITO electrode and the PCDM surface. The results in table 5.1 were obtained immediately after electropolymerisation (Initial) and also after the Al disc was placed on the PCDM film for 30 minutes and than removed prior to the measurement (Zero Bias). After a bias of ± 5 V had been applied to the Al disc overnight, the results presented in tables 5.2 and 5.3 were obtained. The results presented here are for PCDM 1 but are similar to those obtained with the other PCDM films.

Massurament	Surface Pote	ntial (ave.)		Fermi level**	
wicasurement	PCDM (V_{S0}) ITO (V_{S1})	$V_{cpd} = V_{S0} - V_{S1}$	(eV)		
Initial	-0.67	-0.48	-0.19	-4.99	
Zero Bias	-0.75	-0.46	-0.29	-5.09	

 Table 5.1 Surface potential and Fermi level of the PCDM film.

In the measurements the Kelvin probe was scanned from the ITO surface (V_{SI}) to the PCDM surface (V_{S0}) , therefore the contact potential difference (V_{cpd}) is the difference between the surface potentials measured at the ITO and PCDM surfaces.

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Time of	Surface Pot		
measurement (Minutes)	PCDM (V_{S0})	ITO (V _{S1})	$V_{cpd} = V_{S0} - V_{S1}$
0	-0.67	-0.46	-0.21
5	-0.69	-0.47	-0.22
10	-0.70	-0.46	-0.24
15	-0.71	-0.47	-0.24
20	-0.72	-0.47	-0.25
25	-0.72	-0.46	-0.26
30	-0.73	-0.47	-0.26
35	-0.73	-0.47	-0.26
40	-0.73	-0.46	-0.27

Table 5.2 Surface potential and contact potential difference of the PCDM film after5V was applied to the Al.

The Fermi level of the PCDM film under different conditions was calculated using equation 4.1 and assuming that the work functions of ITO, $\phi_{ITO} = 4.8 eV$. From the 'Initial' reading (see table 5.1), the surface potential of the PCDM film is more negative than that of the ITO. This suggests that negative charges accumulated at the PCDM/ITO interface creating a depletion region there as a result of the higher work function of PCDM (4.99 eV). After contacting the surface with the grounded aluminium disc, the surface potential becomes even more negative, possibly reflecting the formation of a depletion region at this upper surface as well. That the negative charge introduced by contacting with the aluminium remains on the surface for any length of time after removing the aluminium is very surprising.

Time of	Surface Pote	$V_{\text{end}} = V_{\text{S0}} - V_{\text{S1}}$	
measurement	PCDM (V _{S0})	ITO (V _{S1})	
0	-0.68	-0.48	-0.20
5	-0.68	-0.49	-0.19
10	-0.69	-0.49	-0.20
15	-0.70	-0.50	-0.20
20	-0.70	-0.50	-0.20
25	-0.71	-0.50	-0.21
30	-0.71	-0.51	-0.20
35	-0.71	-0.51	-0.20
40	-0.71	-0.52	-0.19

Table 5.3 Surface potential and contact potential difference of the PCDM film after -5V was applied to the Al.

Theoretically, the ITO electrode should be able to inject holes into the polymer to neutralise the trapped negative charge at the Al/PCDM interface. However, the depletion region at the PCDM/ITO interface suggests that this interface is likely to be a rectifying contact, and if so, hole injection would be inhibited.

From both table 5.2 and 5.3, it is seen that immediately after the biasing electrode was removed, the contact potential difference, V_{cpd} was similar to the 'Initial' result. However, the behaviour after removing the electrode was different. After removing the +5V electrode the V_{cpd} increased slowly from -0.21 V to -0.27 V (see figure 5.2) i.e. the value seen after removing the grounded electrode. On the other hand, after the -5V electrode was disconnected, V_{cpd} was constant (see figure 5.3). A full explanation of these results is still not available. However, it is believed that upon applying +5V to the aluminium electrode, a depletion region is established at the Al/PCDM interface while that at the ITO interface undergoes some collapse. The net result is a negative charge arising mainly from the aluminium contact. Over time, after removing the electrode, this charge falls but is more than compensated for by the re-establishing of the depletion region at the ITO interface. With -5V applied to the electrode, majority hole carriers are attracted to the upper surface and the depletion region at the ITO expands. Upon removing the Al electrode, holes rapidly re-distribute returning the structure to the 'Initial' condition.

5.6 Capacitance-Voltage Characteristic of PCDM MIS capacitor

To support our argument that a depletion region formed at both interfaces, capacitance-voltage measurements were also conducted. However, our initial results indicated that a simple PCDM diode produced a very noisy C-V plot; therefore, a PCDM MIS device was fabricated by spin coating Photoresist, S1818, (PR) onto the PCDM film prior to Al deposition. The C-V characteristic of this device for PCDM 1 is plotted in figure 5.9 and the results for the other films are similar. When -10V was applied to the ITO electrode, a depletion region was created at the ITO/PCDM interface. Upon scanning the voltage, the capacitance started to increase at -8 V due to the collapse of this depletion region and reached its maximum value at -6V. The capacitance started to decrease when the voltage reached -4V due the growth of another depletion region at the PCDM/PR interface. This depletion region continued

to grow until reaching its maximum width at ~4V. Above this voltage, the measured capacitance was constant.



Figure 5.9 Capacitance-voltage characteristics of the PCDM MIS device at 20 Hz. The voltage was applied to the ITO electrode.

5.7 FTIR spectroscopy

FTIR spectra of films produced in the different cycles are presented in figure 5.10. As can be seen there are differences between the film produced in the first cycle and that produced in the fourth cycle of using the same monomer solution. The FTIR spectra for PCDM 1 and 2 are quite similar with three main peaks at (i) around 1500 cm⁻¹, (ii) 2230 cm⁻¹ and (iii) 3100 cm⁻¹. In PCDM 3, two extra peaks, centred at 2190 cm⁻¹ and ~2900cm⁻¹, start to emerge. In PCDM 4, all peaks in the PCDM 3 were



retained, however, the intensity of the peak at 2190 cm^{-1} increased and the intensity of the peak at 2230 cm^{-1} decreased.

Figure 5.10 FTIR spectrum for PCDM at different polymerisation cycles.

The emergence of the broad peak at ~ 1500 cm⁻¹, which was absent in the spectrum of the CDM monomer, confirms the formation of polymer film. This peak is attributed to changes in π -bonding due to the formation of inter-monomer C_{α} , C_{α} bonds between CDM repeat units in PCDM. The band at 2230 cm⁻¹, is important verification that the CN moiety of the monomer is still present in the polymer (PCDM). Another interesting feature is the band at about 3100 cm⁻¹ which is assigned to the C-H stretch associated with an unsaturated carbon-carbon bond. Some evidence for this is especially obvious in the spectrum of PCDM 1. The extra peak at 2190 cm⁻¹ is possibly due to the presence of CDM monomer in the polymer film. In addition, the peaks at 2900 – 3000 cm⁻¹ must originate from the quaternary ammonium (tetrabutylammonium cation) trapped in the PCDM film during electropolymerisation. PCDM has no saturated C-H moieties in the absence of quaternary ammonium or other contaminants. These important bands and their assignments are summarised in table 5.4 and complete assignment of the bands observed in the FTIR spectrum (figure 5.10) were well documented by Huang and Pickup [7].

Peak (cm ⁻¹)	Designation	Remarks
2900 - 3000	Saturated C-C-H	Peaks in this area are due to the C U
2,000 30000	Saturated, C-C-II	reaks in this area are due to the C-H
	stretch	stretching and vibrations (symmetrical
		as well as asymmetrical) of the
		quaternary ammonium in the PCDM
		with.
2190 and 2230	Cyano moiety, -CN	2230 cm ⁻¹ for CN stretch in polymer
		(PCDM) and 2190 cm ⁻¹ is for CN
		stretch in monomer (CDM) trapped
		inside the polymer film.
3100	Unsaturated, C=C-H	This peak is present in all spectra,
	stretch	because there is only one type of C-H
		stretch in PCDM film where the carbon
		atom forms an unsaturated bond.

Table 5.4 Summary of the H	FTIR spectrum (main pea	ks)
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** All the peak assignments were obtained from [8].

5.8 UV/Vis Spectrum

Figure 5.4 shows a series of UV/VIS spectra obtained from 4 film samples produced successively using the same monomer solution. Also shown is the UV/Vis spectrum for a solution containing the CDM monomer which is included for comparison. The

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only obvious peak in the CDM monomer is the peak centred at around 420 nm. It can be seen that, the main peaks of the PCDM film were at 350 nm, 480 nm and 900 nm.



Figure 5.11 Absorbance of different PCDM film in UV/Vis Spectra and UV/Vis spectrum for CDM solution.

The broad, weak feature centred ~ 900 nm is attributed to the presence of dopant in the polymer film leading to the formation of polaron/bipolaron bands in the PCDM film. A similar interpretation has been presented by Čabala and co-workers [9] for doped PPy. The presence of the 900 nm absorption indicates that the band gap of the polymer is narrow ~ 1.38 eV [3]. This peak does not exist in the UV/Vis spectrum for the CDM solution supporting our argument that this peak is a characteristic of the polymerised film. The peak centred at 350 nm is probably an artefact caused by strong absorption in the ITO below this wavelength.

In conjugated polymers the dominant peaks are normally associated with the π to π^* transitions in the molecule. Typical conjugated polymers exhibit $\pi - \pi^*$ transitions in the visible part of the spectrum. However, the exact position of the absorption band depends on the width of the energy gap between the $\pi - \pi^*$ orbitals. The normal $\pi - \pi^*$ transition of polythiophene occurs at a wavelength in the 450 nm region [10] but shifted slightly in accordance with the substituent attached. Electron withdrawing groups (-CN) shifts the main peak to a longer wavelength (480 nm) in the PCDM film.

5.9 Discussion

During successive polymerisation cycles, changes were observed in the UV/Vis spectra (see figure 5.11). In particular, the 900 nm band became less distinct and disappeared by the fourth cycle. There are a number of possible reasons for this.

Firstly, the concentration of dopant in the monomer solution decreased as the number of polymerisation cycles increased. In this study, there was no replenishment of monomer or electrolytes before the next electro-polymerisation cycle. In an ideal electrochemistry reaction the dopants (cations or anions) should be released back to the solution during the dedoping process that took place immediately after the polymerisation was completed. The spectra for PCDM films produced in the third and fourth cycle demonstrate that this is not the case. The attenuation of the polaron/bipolaron band at 900 nm in successive polymerisation cycles suggests that

less dopant is present in the film. The results here are in agreement with the work reported by Yamamoto et al [11] which shows that electrochemical oxidation led to a new peak at 800–1500 nm in neutral poly(3,4-ethylenedioxythiophene-2,5-diyl).

Secondly, a denser PCDM film may be formed in the first cycle making it difficult to dedope fully. In later cycles, a less dense or thinner film may be formed, thus increasing the efficiency of the dedoping process. From the FTIR spectra, we know that quaternary ammonium counter-cations are trapped in the PCDM film produced in the later cycles. This is not surprising since the dedoping process only removes the BF_4^- dopant ions.

Lastly, when the polymer was doped with BF_4^- , a narrow band gap polymer was produced as seen in polymerisation cycles 1 and 2. However, at cycles 3 and 4, more dimer and other oligomers were present in the supposedly monomer solution and more quaternary ammonium cations became trapped in the film. These trapped cations neutralised the tetrafluoroborate anions in the polymer and as a result, they will not be free to complex with the polymer and were unable, therefore, to initiate the formation of polarons and bipolarons in the PCDM film. Consequently, PCDM films produced from such 'monomer' solution would not exhibit low energy transitions between polaron bands.

The presence of the quaternary ammonium cations in the PCDM films produced in the later cycles was confirmed by the FTIR analysis. As the number of polymerisation cycles increased, more and more dimer or other oligomers (such as

the trimer, etc) are likely to be present in the monomer solution. Therefore the chemical equilibrium in the solution as well as the growth of the polymer film is likely to be disrupted. For example, oligomers in the monomer solution could become part of the growing film, trapping other monomer molecules as well as quaternary ammonium counter-cations (tetrabutylammonium cations).

The decrease in the observed currents in the later film produced successively from the same monomer solution correlates well with the spectroscopic data which indicate a reduction in dopant concentration in the film, albeit it through compensation of the BF_4^- ions with alkyl ammonium counter-ions. On the other hand, the strong memory effect can be associated with polymer produced in the early stages of electrodeposition using a freshly prepared solution. In such a polymer the polaron/bipolaron band is clearly formed due to doping by BF_4^- . The ions trapped in the film create negative space charges in the polymer near the electrode/polymer interface. These space charges play a vital role in polymer memory device as shown in the earlier studies [2, 12]. Several research groups [13 –19] have reported that the space charges trapped in the polymer film accumulated at the polymer/metal interface and screen the electric field, which in turn limits the current injection.

When negative bias is applied to the Al top electrode, the depletion region is expected to grow. Additionally, BF_4^- ions were also repelled from the interface and consequently, the lower ion concentration led to a wider than expected depletion region. As a result, the carrier injection was blocked and the current becomes barrierlimited, therefore the device was effectively in a low conductance state. On the other hand, when positive bias was applied to the Al electrode the depletion region width

decreases. Furthermore, BF_4^- ions drifted to the PCDM/Al interface, thus increasing the ion concentration at the interface leading to a thinner than expected depletion region. In this case, the depletion width decreased until sufficiently thin to allow tunnelling to occur across the barrier. Therefore the conduction becomes bulklimited and the device is in its high conductance states. These two conductance states were referred to as a memory effect by Mills et al [1, 2]. In freshly prepared film, the counter-ions were believed to be absent, therefore BF_4^- effectively controlled the carrier injection at the interface and as a result, two conductance states were observed in this device. In this study it was shown that the memory effect in PCDM 1 was slightly higher than the results obtained by Mills and co-workers [1]. In the later sample, some of the counter-ions were also trapped in the film which bound BF_4^- ions and consequently the memory effect started to decrease in PCDM 2 and totally diminish in PCDM 4 when the concentration of the counter-ions and $BF_4^$ ions are equal.

In addition, from the surface potential measurement and PCDM MIS C-V plot, there is also a possibility that a rectifying contact is present at the ITO/PCDM interface. The basic mechanisms at the interface are the opposite of that at Al/PCDM interface, i.e. the depletion region at this interface become thinner when negative voltage was applied to the Al electrode and vice versa. This might explain the absence of rectification in the current-voltage characteristics of the PCDM diode.

The complex admittance plot of the PCDM 1 diodes show that this device had a single relaxation time following the model presented in section 3.2.2. The extension

of the dispersion in the AC characteristics of the PCDM film prepared in the later cycles might indicate the diffusion of the ions. Some evidence for this is obtained from a Bode plot of the AC data. Figure 5.12 shows the $\log |Z|$ versus log frequency of different PCDM films.



Figure 5.12 Bode plots of different PCDM films.

Interestingly, the slope of PCDM 1 plot in the frequency range of 200 Hz to 1 kHz is close to -1 which reflects the presence of pure R-C elements in the equivalent circuit. On the other hand, the slope of PCDM 2 and 3 in the frequency range of 200 Hz to 100 kHz, is closed to -0.5 and identical to that expected for a Warburg impedance. Therefore we believe that in this frequency range, ionic (alkyl ammonium counter-cations) diffusion from the bulk to the depletion region may be dominant.

5.10 Summary

Successive electrodeposition of polymer films from the same monomer solution led to systematic changes in the spectroscopic and electrical characteristics of each PCDM film. From dc characterisation, two main differences were observed. Firstly, the memory effect was reduced in the later films even disappearing in the PCDM film produced in the fourth cycle. Secondly, the observed currents were also generally lower in the later film suggesting much reduced doping of the polymer. The dispersion in the admittance of the device clearly indicates the presence of a depletion region at one of the electrode/polymer interfaces. UV/Vis spectroscopic analysis showed that the dopants (BF_4^-) were only sufficient to form a polaron/bipolaron band in the first two films which had a lower energy gap compared to the later films. Finally, FTIR spectra indicated that the quaternary ammonium counter-ions are trapped in the PCDM films produced in the later electropolymerisation cycles. These would neutralise the doping effect of the BF_4^- anion.

Therefore, it is suggested that the presence of BF_4^- and the absence of the counterions are essential for the observation of the memory effect in PCDM. In the absence of the counter-ions, BF_4^- effectively behaves as a space charge. Thus under forward bias, BF_4^- is attracted to the ITO/PCDM interface and the depletion region becomes thinner than expected leading to a 'high' conductance state. Conversely, under reverse bias, BF_4^- is repelled from the interface and the depletion region became wider than expected. As a result, the device was driven into the 'low' conductance state. On the other hand, as indicated by the FTIR spectra, the effect of BF_4^- is shielded in the later films by trapped alkyl-ammonium, which explained the disappearance of the memory effect in the corresponding PCDM films.

The results from the ac measurements show that there should be a rectifying contact at the metal/polymer interface and hence should show significant rectification in dc results. However, the expected rectification was absent in the dc characteristics of the PCDM film which might suggest that both electrodes, ITO and Al, formed a rectifying contact with PCDM film. This assumption was supported by the result from surface potential measurement and the C-V characteristic of the PCDM MIS structure which showed that there is a possibility that depletion regions were formed at both interfaces. Based on the work function difference between ITO and Al, the barrier heights at these interfaces were believed to be significantly different which might explain why a small degree of rectification was observed in dc characteristics especially in PCDM 1.

Finally, the diode fabricated in this study did indeed show a very good memory effect provided the PCDM film was electropolymerised from a fresh monomer solution. However, this memory effect disappeared in the diode fabricated from the PCDM film prepared successively from the same monomer solution. Therefore, it is concluded that fabricating a memory device from electrodeposited PCDM materials is unlikely to be commercially viable. Other film deposition technique such as spin coating might be possible only if CDM monomer is soluble in a less harmful solvent. To our knowledge, however, CDM monomer only fully dissolves in nitrobenzene. The failure to fully manipulate the PCDM material into a viable memory device
prompted a change of direction, to the fabrication of a flash memory device from the well-known organic semiconductor, i.e. P3HT as described in chapter 6.

5.11 References

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6.1 Introduction

In this chapter we focus our attention on the electrical characterisation of a series of device designs leading ultimately to the floating gate memory device. Firstly we report the results of both dc and ac characterisation of the ITO/P3HT/Al Schottky diode in section 6.2, followed by the metal-insulator-metal (MIM) structure, ITO/PSQ/Au in section 6.3. The results from a simple metal-insulator-semiconductor-metal (MISM) structure composed of ITO/PSQ/P3HT/Al are presented and discussed in section 6.4 and finally the results from the floating gate memory device, ITO/PSQ/Au/PSQ/P3HT/Al are presented and discussed in section 6.4 and finally the results from the floating gate memory device, ITO/PSQ/Au/PSQ/P3HT/Al are presented and discussed in section i.e. starting from negative or positive bias respectively. It is worth noting that the sweep voltage ranges were varied for the different types of device, and will be highlighted in the appropriate sections.

6.2 ITO/P3HT/Al Schottky Diodes

The AC and DC characteristics of Schottky diodes formed by sandwiching P3HT between an ITO bottom gate electrode and an Al top electrode are well-documented [1, 2]. Nevertheless, for completeness, we have also studied such diodes. In this chapter, therefore, we will present only a brief description of the results of the P3HT Schottky diodes and compare them with previously documented literature. The DC and AC characteristics of the P3HT Schottky diode provide an important guide for comparison with the final flash memory device results.

6.2.1 DC Characteristics

Figure 6.1 shows the current-voltage characteristics of the P3HT Schottky diode when the voltage was swept from -3 V to 3 V and vice versa. The current was slightly higher when the bias was swept from -3 V to 0 V compared to the opposite sweep direction, however in the positive voltage region, the current was virtually independent of sweep direction.



Figure 6.1 Current flowing in the P3HT Schottky diode as a function of voltage applied to the ITO electrode.

As can be seen from figure 6.1, the I-V characteristics of the P3HT diode displayed the expected rectification and the turn-on voltage of the P3HT diode was found to be ~0.6 V. Additionally, the rectification ratio was estimated to be ~ 10^4 at ± 1 V and ~ 10^6 at ± 2 V. These values are in agreement with the turn-on voltage and rectification ratio of the FeCl₃-doped P3HT Schottky diode studied by Kuo et al [1]. Above \sim 1.3V the rise in current is much slower compared to the slope in the range 0.6 to 1.3 V where the current increases rapidly. The latter is due to the reduction in depletion width at the interface and an increase in holes injection. Above 1.3 V, there is virtually no depletion region at the interface; therefore the current becomes bulk limited due to the P3HT resistance.

6.2.2 AC Characteristics

Although, the P3HT Schottky diode has been studied extensively [1–8], information on the AC characteristics of this device is very scarce, except in the case of poly (3methylthiophene) (P3MET) [9], a related thiophene-based polymer. The frequency dependence of the capacitance of a typical Schottky diode produced in the present work is shown in figure 6.2. Below 2.5 kHz, the capacitance is generally constant but at higher frequencies, the measured capacitance decreases to a lower, constant value. Furthermore, as the applied DC bias changes from positive to negative, the low frequency capacitance falls to the same value as that seen at high frequency.

This behaviour is readily explained using the equivalent circuit in section 3.2.2. The polymer Schottky diode is divided into two regions, a depletion region and a bulk region. At low frequencies, where $\omega \tau_R \ll 1$, the bulk resistance (R_B) shunts the bulk capacitance (C_B) of the P3HT layer, thus the capacitance of the depletion region dominates the overall capacitance. Therefore, the measured capacitance at these frequencies is the capacitance of the depletion region at the particular bias voltage. As the frequency increases to ~ 1 kHz, the reactance of C_B approaches that of R_B , and

eventually dominates, so that the contribution of C_B to the measured capacitance becomes significant, leading to the observed dispersion between 1 kHz and 60 kHz. At high frequencies, when $\omega \tau_R >>1$, the measured capacitance is the series sum of the depletion and bulk capacitances.



Figure 6.2 Capacitance-frequency characteristics of the P3HT Schottky diodes for different voltages applied to the ITO electrode.

When negative voltage was applied to the Al electrode, the device was driven into reverse bias and the depletion region at the interface grew wider. As a result the capacitance in the low frequency range became very low. From figure 6.2, it is seen that upon applying -2 V, the device was fully depleted with the depletion region extending to the ITO/P3HT interface. On the other hand, when positive voltage was applied to the Al electrode, the device was driven into forward bias, the depletion region width decreased and its capacitance increased. This behaviour was described in detail by Taylor and Gomes [9] for their P3MET Schottky diode.

Figure 6.3 shows the loss-frequency characteristics of the Schottky diode with different biases applied to the Al electrode. At frequencies below 3 kHz, except when positive voltages were applied to the Al electrode, the loss, G/ω was low. The loss at low frequencies was exceptionally high especially when +2V was applied to the Al electrode. This corresponds to forward bias and a high conduction current through the depletion region. On the other hand, under high reverse bias (-2V) the loss was low and almost constant throughout the frequency range except for a slight increase at high frequencies caused by the contact resistance. As predicted in section 3.2.2, equation (3.16), when the depletion and bulk regions co-exist, the loss goes through a maximum at a frequency determined by equation (3.17).



Figure 6.3: Loss-frequency characteristics of P3HT Schottky diodes for different voltages applied to the ITO electrode.

A close look at the loss versus frequency characteristics of the P3HT device reveals that the relaxation frequency of the device remains constant for different values of forward bias. As a first approximation, the relaxation frequency is equal to $\frac{1}{2\pi R_b C_d}$. As forward bias increases, C_d is expected to increase and relaxation frequency to decrease. However, to counter this, as can be seen in figure 6.1, at high forward bias, R_b decreases. Additionally, as the depletion region becomes thinner as the forward bias increases, R_d also decreases. Thus the relaxation frequency now follows equation (3.14).

The Cole-Cole plot in figure 6.4 is seen to depart from a perfect semicircle which implied that the P3HT Schottky diode produced in this study has a distribution of relaxation times rather than the single relaxation time as represented by a Debye-like dispersion [10]. Departure from the semicircular plot might be due to the disordered nature of the P3HT structure thus promoting dispersive transport in the bulk.

The depletion region capacitance (C_d) and the total film capacitance (C_s) may be deduced by extrapolating the low frequency and high frequency capacitance data respectively to the horizontal axis in figure 6.4. Based on the dielectric constant of 3.2 for P3HT [11] and the top electrode area of 9.62 x 10⁻⁶ m², the depletion region and the film thicknesses at different voltages may be calculated by using the equation for parallel plate capacitor, $C = \frac{\varepsilon \varepsilon_0 A}{d}$, where C is the capacitance, ϵ is the relative permittivity of the polymer, ϵ_0 is the permittivity of free space, A is the top electrode area and d is the thickness.

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Figure 6.4 Cole-Cole plot of the P3HT Schottky diodes.

Table 6.1 shows the depletion and bulk thicknesses for the different voltages. From this table it is clearly seen that the P3HT is almost fully depleted when -2 V was applied to the Al electrode. The overall film thickness calculated from this measurement was \sim 227 nm which is within the film thickness range of 200 – 400 nm prepared from 1% wt/wt P3HT solution [12].

Capacitance measurements as a function of voltage were also conducted for the P3HT Schottky diode at a fixed frequency of 1 kHz. Figure 6.5 shows the capacitance-voltage characteristics of the diode when the voltage was swept from -2 V to 2 V (Diode-n) and from 2 V to -2 V (Diode-p). The C-V characteristic is seen to be independent of sweep direction and simply reflects the growth and collapse of the depletion region. It may be deduced, therefore, that dopant migration does not occur in the time scale of the measurement. Furthermore, deep trapping effects can also be discounted.

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Applied voltage (V)	<i>C</i> _{<i>d</i>} (nF)	<i>C_b</i> (nF)	Depletion thickness (nm)	Bulk thickness (nm)
2.0	19.0	1.28	14.3	212.9
1.0	10.7	1.35	25.4	201.8
0.5	6.0	1.50	45.4	181.7
0	4.2	1.68	64.9	162.2
-0.5	1.5	6.0	181.7	45.4
-1.0	1.4	8.4	194.6	32.4
-2.0	1.3	15.6	209.6	17.5

Table 6.1 Depletion and bulk thickness at different applied voltages.

*All capacitance values were estimated from figure 6.4.



Figure 6.5 Capacitance-voltage characteristics of P3HT Schottky Diodes at 1 kHz.

The data in figure 6.5 is replotted in figure 6.6 as C^{-2} versus V, following the standard Mott-Schottky analysis. The slope of the linear portion of the plot together with equation 3.4 yields an acceptor doping density, N_A , of the P3HT film of 1.1 x 10^{16} cm⁻³. This is in good agreement with the doping density in P3HT deduced by Torres et al [12], in their studies of MIS structures incorporating P3HT. In their studies of Schottky diodes from electro-deposited P3MET, Taylor and Gomes [9] estimated doping densities to be in the range of 4.6 X 10^{16} cm⁻³ to 6.0 X 10^{19} cm⁻³. From figure 6.6, the built-in potential (ϕ_i) of the diode is estimated to be ~0.4 V.



Figure 6.6 Mott-Schottky plot of the P3HT Schottky diode.

6.3 Metal-insulator-metal (MIM) device

6.3.1 Introduction

The insulator used to fabricate the final flash memory device was polysilsesquioxane (PSQ). In this section, the electrical characteristics of the polysilsesquioxane (PSQ) insulator will be presented. The samples were in the form of an MIM structure in which the two electrodes were ITO and Au. Although some reports on the electrical characteristics of the PSQ MIM structures appear in the literature [13], surprisingly, most authors only used the PSQ film as a low dielectric constant material for their final device e.g. in organic field-effects transistors [14], ceramic films [15] and high performance coating and low dielectric constant interlayer for electronic devices [16]. Therefore, the results from this section were needed to determine the stability and leakage resistance of the PSQ film fabricated in this study.

6.3.2 DC Characteristics of MIM device

The DC characteristics were measured by sweeping the voltage applied to the ITO electrode through the range -40 V to +40 V in 0.5 V increments. The device current was measured at the gold top electrode. The measurement was started at room temperature (\sim 20°C) with subsequent data being obtained at 10°C intervals until the temperature reached 130°C. However, for clarity, in figure 6.7 we only plot the results obtained at room temperature, 50°C, 80°C, 100°C, and 130°C.



Figure 6.7 Current – voltage characteristics of the PSQ MIM device at different temperature (RT is the current measured at room temperature).

As expected, the I-V characteristics of the MIM structure are basically symmetrical for the two sweep directions, because both the top and bottom electrodes are made from materials with almost identical work function (ϕ_m) , i.e. ϕ_m (ITO) = 4.8 eV and ϕ_m (Au) = 5.0 eV. If the temperature dependence of the current in figure 6.7 follows an Arrhénius-type law i.e.,

$$J = J_0 \exp\left(-\frac{E_a}{kT}\right)$$

where J is current density, E_a is the activation energy, k is Boltzmann's constant and T is temperature in Kelvin, then the data should yield a linear plot when log J is plotted against 1/T. In figure 6.8 some of the data from figure 6.7 is plotted in this

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form for the situations when the voltage was swept from (a) -40 V to 40 V, and (b) 40 V to -40 V.



(a)



(b)

Figure 6.7 Arrhénius plot showing the effect of temperature on the current flowing through MIM device at different voltages, with voltage sweep (a) -40 V to 40 V, and (b) 40 V to -40 V with temperature ranges between $25^{\circ}C$ to $60^{\circ}C$ (dotted-line) and $70^{\circ}C$ to $130^{\circ}C$ (solid line).

As can be seen, the plots show two distinct regions; a region that is weakly dependent on temperature in the range 25°C to 60°C, and a second region of almost linear slope between 70°C to 130°C. From the asymptotic values of the slopes we can deduce activation energies relevant to the extremes of temperature investigated. These values are tabulated in table 6.2.

Table 6.2 The activation energy of the PSQ at different voltages and for two temperature ranges.

	Activation Energy (eV)			
	25°C to	25°C to 60°C		130°C
Voltage (V)	n	р	n	Р
-5	0.30	0.41	0.99	0.92
5	0.31	0.38	0.98	1.00
-10	0.27	0.39	0.96	1.00
10	0.30	0.33	0.95	1.00
-20	0.26	0.38	0.92	0.94
20	0.30	0.31	0.93	0.95
-40	0.25	0.30	0.88	0.88
40	0.29	0.27	0.88	0.88

From this table, it is seen that the activation energy was much lower in the temperature range of 25 °C to 60 °C compared to 70 °C to 130 °C. For example, the activation energies of the PSQ film at -10 V and 10 V when the voltage was swept from -40 V to 40 V (n) were 0.96 eV and 0.95 eV respectively in the temperature range 70 °C to 130 °C compared to 0.27 eV and 0.30 eV at lower temperatures.

Interestingly, the activation energy decreased slightly when the voltage was increased, irrespective of the voltage polarity, which is consistent with the Schottky or P-F conduction models (we will return to this point later).

6.3.3 AC Characteristics of MIM device

The capacitance of the PSQ films was also measured over a range of frequency, temperature and applied DC bias. A typical set of data obtained for temperatures ranging up to 110° C and with 20 V applied across the MIM structure is given in figure 6.9. Figure 6.10 shows the data obtained at 100° C for voltages in the range -40 V to 40 V.



Figure 6.9 Capacitance-frequency characteristics of the MIM device at 20V for different temperatures.

From these figures, the capacitance is seen to be independent of frequency, and applied voltage over the whole measurement ranges (20 Hz < f < 1MHz, and -40 V to +40 V). However, as seen in figure 6.9, capacitance decreases slightly as the temperature increased. The reduction in capacitance was also observed when -20 V was applied to the MIM device. The small drop at the highest frequencies is believed to arise from a contact resistance effect.



Figure 6.10 Capacitance-frequency characteristics of the MIM device at 100°C for different applied voltages (all curves ranging from -40 V to 40 V are identical).

As expected for a good insulator, the dielectric loss in the MIM structure is almost zero for frequencies below ~10 kHz (figure 6.11 and 6.12). The increasing loss above this frequency is caused by the presence of a contact resistance. The small increase in loss at these frequencies upon increasing temperature suggests an increase in the resistance. This increment was absent when different voltages were applied to the MIM structure at 100°C which suggests that the resistivity of PSQ and the contact resistance are independent of the applied voltage (voltage ranges from - 40 V to + 40 V).



Figure 6.11 Loss-frequency characteristics of the MIM device at 20V for different temperatures.



Figure 6.12 Loss-frequency characteristics of the MIM device at 100°C for different applied voltage (all the loss curves ranging -40 V to 40 V are exactly the same).

6.3.4 Discussion

Since the thickness of the PSQ film is unknown, we are unable to calculate the dielectric constant from the high frequency capacitance in figure 6.9. Instead, using the relationship $C = \frac{\varepsilon_0 \varepsilon_r A}{d}$, we calculate the value of $\frac{\varepsilon_r}{d}$ which will be used in estimating the dielectric constant from the Schottky and P-F plots later. Using the capacitance measured at 100 kHz and assuming an area of 9.62 mm², $\frac{\varepsilon_r}{d}$ is calculated and combined with data from Schottky and Poole-Frenkel plots in order to extract a value for ϵ_r (see table 6.3). From the Arrhénius plots in figures 6.8, the conduction through the PSQ film might follow either the Schottky or P-F models. Therefore, to test these two conduction mechanisms, we plot ln J and ln J/V against V^{1/2} as shown in figure 6.13 for voltage sweeps from 40V to -40V (in the opposite sweep, the plots were almost identical).

The ln J and ln J/V plots exhibited a good linear relationship with $V^{1/2}$ for all temperature ranges and sweep directions at high applied field but did show some curvature away from linearity at lower fields. At these lower applied fields, the current was linear in the applied field indicating ohmic behaviour. From equation (2.11), the experimental barrier lowering coefficients, β_{exp} = slope x kT. The Schottky

and Poole-Frenkel lowering coefficient,
$$\beta_{SC} = \left(\frac{q^3}{4\pi\varepsilon_0\varepsilon_r}\right)^{1/2}$$
 and $\beta_{PF} = 2\beta_{SC}$, [13]

respectively from which values of $\varepsilon_r d$ were calculated and the dielectric constants of the PSQ film at different temperatures were estimated (table 6.3).



Figure 6.13 Schottky (a) and Poole-Frenkel plots of the MIM structure at different temperature at voltage sweep from 40 V to -40 V.

	Dielectric Constant, ϵ_r .		
Temperature (°C)	Schottky plot	Poole-Frenkel plot	
25	4.3	15.8	
60	5.4	28.6	
80	5.8	21.9	
100	6.3	26.6	
130	6.4	36.0	

Table 6.3 Calculated dielectric constant of the PSQ film at different temperatures when the voltage was swept from 40 V to -40 V.

As can be seen from table 6.3, the dielectric constant estimated from the P-F plot is exceptionally high compared to that deduced from the Schottky plot. From the literature, the room temperature dielectric constant for PSQ film is accepted to be in the range 2.0 to 4.0 [13, 14-20], which is significantly lower than the values obtained even from the Schottky plot, except at room temperature. Assuming that conduction through the PSQ insulator at high field satisfies the Schottky conduction mechanism, the film thicknesses for different temperatures were estimated and tabulated in table 6.4. The decrease in capacitance shown in figure 6.9 is insignificant compared to the increase in calculated film thickness and dielectric constant. The film thickness and dielectric constant increased by more than 50%, whereas the measured capacitance only decreased by about 2% when the PSQ film was heated from room temperature up to 130°C. Therefore, it is concluded that the conduction through the PSQ film does not fully obey the Schottky model. For example, space-charges in the insulator may be causing the field at the injecting contact to depart from the average field.

Capacitance (pF)	PSQ Thickness (nm)
756	484
750	613
745	662
740	725
737	739
	Capacitance (pF) 756 750 745 740 737

 Table 6.4 Calculated PSQ film thickness at different temperature.

The bulk resistivity (ρ) of the insulator can be calculated and in table 6.5 we give the values measured at room temperature and 130°C and at two voltages 0.5V (1.8 MV/m) and 40V (143 MV/m). The values of resistivity deduced above, confirm that good quality insulating films of PSQ can be prepared. These values are comparable to amorphous SiO₂. For example, Chen and co-worker [17] report that the resistivity of SiO₂ films was 5 x 10¹⁵ Ω cm at 5 MV/m.

Table 6.5 Bulk resistivity of the PSQ film at different electric fields and temperatures.

Electric Field (MV/m)	Bulk Resistivity (Ω cm)		
Electric Field (NI V/III)	Room Temperature	130°C	
1.0	9.5 x 10 ¹⁵	2.9 x 10 ¹⁵	
82	$9.3 \ge 10^{12}$	$1.6 \ge 10^{12}$	

6.4 Metal-Insulator-Semiconductor-Metal (MISM) Device

For the purpose of comparison and prior to fabricating the final flash memory device, a Metal-Insulator-Semiconductor-Metal (MISM) structure was fabricated by sandwiching the PSQ/P3HT bilayer between an ITO bottom gate electrode and an Al top electrode 1.8 mm in diameter. The behaviour of this structure is described below.

6.4.1 DC Characteristics of the MISM Device.

The DC measurement was started by sweeping the voltage on the ITO electrode from -20 V to 20V stepped in increments of 0.2V every 1s. The voltage sweep was then repeated immediately but in the opposite direction. The current-voltage characteristic of the MISM device is shown in figure 6.14 and 6.15 and is generally similar to the current-voltage characteristics of the Schottky diode (section 6.2.2) with a turn-on voltage of \sim 1.0 V.

However, when the data is replotted in semilog form (figure 6.15) the differences between the Schottky diode and the MISM device become apparent. Although the same order of magnitude at the lower voltages, the reverse currents in the MISM device increase much more slowly with increasing reverse bias than for the Schottky diode. For example, at -3V, the device currents are ~9 x 10^{-8} A/m² and 1.8 x 10^{-7} A/m² (depending on sweep direction) for the MISM device and 5 x 10^{-5} A/m² for the Schottky diode.



Figure 6.14 *Current* – *voltage characteristics of the MISM device. Voltages were applied to the ITO electrode.*



Figure 6.15 Log current density versus voltage applied to the ITO electrode for the MISM device showing a rectification of more than 3 orders of magnitude.

Similar behaviour is observed in forward bias, with the forward current in the Schottky diode rising to $\sim 20 \text{ A/m}^2$ at +3 V, in contrast to a forward current of $\sim 6 \text{ x}$ 10^{-4} A/m^2 in the MISM device. The smaller currents and reduced rectification in the MISM device compared to the Schottky diode is consistent with the presence of an insulating layer blocking current flow through the device.

6.4.2 AC Characteristics of the MISM Device

6.4.2.1 Frequency Dependence

The capacitance of the MISM device was measured over a wide range of frequencies and for different bias voltages. To an extent, this repeats the previous study by Torres [21] on the same device configuration. However, in the present study the ohmic gold contact to the semiconductor has been changed to a rectifying aluminium junction. It was necessary therefore to establish the AC behaviour of the present MISM device in order to provide a reference for discussing the results obtained from the flash memory device. The frequency dependence of capacitance and loss for the device is shown in figures 6.16 and 6.17. The plots show almost classic Maxwell-Wagner behaviour, with a relaxation frequency just below 10⁵ Hz. As expected, the low frequency capacitance of the structure is sensitive to the applied bias because of the growth/collapse of the depletion regions at the aluminium/PSQ interfaces with the P3HT.

When the bias applied to the ITO electrode was increased from 0 to -1 V, the low frequency capacitance increased by \sim 15 pF. Further increases in negative bias

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caused the capacitance to decrease. Such behaviour suggests that, at zero bias the semiconductor interfaces with the Al and the gate insulator are both in depletion. Negative bias applied to the ITO should drive the P3HT/PSQ interface into accumulation while increasing the depletion region at the P3HT/ Al interface.



Figure 6.16 Capacitance versus frequency characteristics of the MISM device for different voltages applied to the ITO electrode.

The initial increase in capacitance is consistent therefore with the collapse of the depletion region at the insulator interface while the subsequent decrease reflects the expansion of the depletion region at the Al electrode. When increasing positive voltages are applied to the ITO electrode, the device capacitance decreases steadily, reflecting the growth of the depletion region at the PSQ interface and the collapse of that at the Al electrode.

From figure 6.17 we see that the growth and collapse of the two depletion regions results in a shift in the device relaxation frequency. With positive bias applied, the relaxation frequency moves steadily to higher values, 60 kHz to 120 kHz, following the prediction of the model presented in section 3.3.4 and equation (3.31) i.e., a consequence of the expanding depletion region at the PSQ interface. For negative applied voltages, the relaxation frequency moves slightly towards lower frequencies.



Figure 6.17 Loss versus frequency characteristics of the MISM device for different voltages applied to the ITO electrode.

Following a similar argument to that developed for positive bias, we assume this reflects the collapse of the depletion region at the PSQ interface. Since the behaviour is dominated by the depletion region at the PSQ interface, presumably the collapse (growth) of the depletion region at the Al electrode for positive (negative) bias is much less sensitive to the applied voltage.

The capacitance and loss data from figures 6.16 and 6.17 are replotted in the complex plane (Cole-Cole plot) in figure 6.18. As expected, the data shows the presence of one main relaxation process due to the effect of the bulk polymer. The beginning of a second dispersion arising from a contact resistance is also visible at high frequency. At the lowest frequencies, conduction through the PSQ gives rise to an increasing loss. The main relaxation is described by arcs of different radii for each voltage applied. Departure from the semicircular plot expected for a single relaxation time is probably caused by dispersive transport in the bulk of the P3HT [11].



Figure 6.18 Loss versus capacitance characteristics (Cole-Cole plot) of the MISM device under different bias voltages applied to the ITO electrode.

Assuming that at -1 V, where maximum capacitance is observed, the reactance of the depletion regions is negligible, then the measured capacitance at low frequencies \sim 167 pF is that of the gate insulator. The corresponding insulator thickness is then calculated to be \sim 570 nm assuming that the calculated PSQ dielectric constant in section 6.3 is correct. At high frequencies, extrapolation of the main relaxation

process to the horizontal axis yields a capacitance, ~104 pF, corresponding to the series sum of the insulator and semiconductor capacitances. Assuming $C_{in} = 167$ pF then the bulk semiconductor capacitance is 276 pF corresponding to a thickness of ~ 260 nm. Returning now to the voltage-dependent low frequency capacitances, we may estimate in each case the capacitance of the depletion regions and the corresponding width of the depletion regions. These are given in table 6.5.

Applied Voltage (V)	C _{LF} (pF)	C _D (pF)	Depletion Width (nm)
>-5	161	4481	39.5
-4	162	5410	13.1
-3	163	6805	7.9
-2	164	9129	10.6
-1*	167	œ	0
0	153	1825	16.1
1	141	906	79.5
2	136	732	98.4
3	132	630	114.6
4	127	530	136.0
5	124	482	149.8
10	110	322	223.8
15 & 20	104	275	262.1

Table 6.5 Depletion width estimated from figure 6.4.5 at different applied voltage.

* Assuming that no depletion region exist at Al/P3HT interface.

 C_{LF} is the low frequency capacitance.

As deduced earlier, for voltages > -1V the dominant depletion region is at the P3HT/A1 interface. For more positive values that at the P3HT/PSQ interface dominates. Although the values estimated for the thicknesses of the PSQ and P3HT layers are reasonable, they are significantly larger than previously estimated from separate electrical measurements on the PSQ MIM structure (488 nm) and P3HT/A1 Schottky diode (227 nm). Since such differences would not be expected given the identical preparation conditions, some doubt must be cast on the assumption that the depletion region capacitances can be neglected when -1 V is applied to the structure.

6.4.3.2 C-V Plot

In addition to investigating the frequency-dependence, the device capacitance was also measured as a function of applied voltage. The measurement was made by sweeping the voltage applied to the ITO electrode from 20V to -20V and vice versa, stepping the voltage in increments of 0.5 V per second. The results obtained at a modulating frequency of 1 kHz are shown in figure 6.19. From our previous discussion, depletion regions are expected to be present at either the Al/P3HT interface (when negative voltages were applied) or the PSQ/P3HT interface (for positive voltages). Figure 6.19 shows this to be the case.

In the voltage range -1 V to 20 V, the depletion region at the PSQ/P3HT interface dominates and grows to a maximum value at \sim 13 V. Above this voltage, the depletion region stops growing due to the P3HT layer becoming fully depleted. Assuming the maximum capacitance at -1.5 V is equal to the insulator capacitance, the depletion region capacitance when the P3HT layer is fully depleted was estimated to be \sim 307 pF. Therefore the maximum depletion region width was calculated to be ~234 nm which is close to the P3HT thickness calculated from the Schottky diode structure in section 6.2.2 (page 180). The data from figure 6.19 also indicates that the CV result for the MISM device is independent of the sweep direction. This shows that there are no long-lived charges at the interface. For the small range between 0 and -1 V, depletion regions are present at both interfaces with that at the PSQ/P3HT interface dominating. For more negative voltages, the depletion region at the Al/P3HT interface dominates and continues to grow to a maximum width (~39.5 nm, see table 6.5) at ~-8 V. From -8 V to -20 V, the depletion region at Al/P3HT failed to grow wider probably due to current leakage through the depletion region at the higher applied field.



Figure 6.19 Capacitance versus voltage characteristics of the MISM device at 1 kHz with the bias applied to the ITO electrode from -20 V to 20 V (n) and 20 V to -20 V (p).

6.5 Floating Gate Memory Device

6.5.1 Introduction

In the memory device, the ITO electrode acts as a control gate while the thin layer of Au acts as a floating gate, where the charge will be stored. The top electrode is comprised of a circular Al electrode 1.8 mm in diameter. For simplicity, the thickness of each of the polymer layers forming the memory stack was assumed to be the same as that of the corresponding layer prepared separately. The true overall thickness of the stack, however, may be much lower so that the second layer of PSQ (next to the P3HT film–PSQ2) may be much thinner than the first PSQ layer (PSQ1).

6.5.2 DC characteristics of the Flash Memory device

The DC behaviour of the flash memory device was characterised by measuring the current and the capacitance as a function of applied voltage. All the measurements were started by sweeping the voltage from negative to positive voltages and vice versa. The voltage for the DC measurement was applied to the Al electrode.

6.5.2.1 Current-Voltage Characteristics

A typical current-voltage plot of the flash memory device at the measurement ranges of -20 V to +20 V is shown in figure 6.20 (a) displaying a hysteresis only when the positive bias was applied to the Al electrode.



Figure 6.20 Current – voltage characteristics of the memory device at different voltage sweeps with voltage applied to the Al electrode. (a) Combination of data with inset displaying the threshold voltage. Also shown is the positive region of the voltage sweep (b) -5V to 5V and (c)-10V to 10V.

The threshold voltages were shifted to a lower value when the measurement ranges were reduced to -5 V to +5 V and -10 V to +10 V respectively (see figure 6.20 (a)-inset). Interestingly, the hysteresis observed when the voltage was swept from -20 V to +20 V and vice versa was absent in the voltage range of -5 V to +5 V (see figure 6.20 (b)) and started to appear when the sweep range was increased to -10 V to +10 V (see figure 6.20 (c)).

In this study, the current-voltage measurements of the flash memory device were repeated over a number of cycles using the same device as well as a different device. Figure 6.21 shows the combination of the current-voltage characteristics of the memory device and from this figure, we suggest that the memory effect observed in this study is reproducible.



Figure 6.21 Current-voltage characteristics showing two voltage cycles for five different devices. Arrow indicates voltage sweep direction and inset shows the curve for two different measurement cycles of the same device.
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However, as seen in figure 6.21, the current-voltage curves were slightly shifted either to lower or higher voltages. This shift may be due to a local variation of the PSQ thickness because the current-voltage characteristic (figure 6.21 (inset)) of the same device measured via the same top electrode shows an almost identical curve.

6.5.2.2 Capacitance-Voltage Characteristics

Figure 6.22 shows the capacitance-voltage characteristic of the memory device whilst the bias applied to the aluminium electrode was swept from -20 V to 20 V and vice versa. The C-V measurement was started by sweeping the voltage from 0 V to 20 V with a 5 minute interval before proceeding to the subsequent sweep. There is a clear hysteresis in the capacitance-voltage characteristics of the memory device which was absent in a typical MISM device (figure 6.19).

The capacitance decreased sharply when the voltage was swept from 0 V to -20 V, and reached its minimum value of ~ 160 pF at -8 V below which the capacitance is constant. When the voltage sweep was started from -20 V to 20 V, the capacitance remains minimal for the voltages more negative than -13.5 V. Then, when sweeping to a less negative voltages, the capacitance increased rapidly between -12 V and -4.5 V after which the capacitance continued to increase slowly until reaching its maximum value of ~300 pF at 13.5 V. Interestingly, when the sweep was reversed, the capacitance remained high above 13.5 V and then started to slowly fall and below ~3 V, the capacitance decreased rapidly until ~4.5 V. The capacitance reached a minimum value at ~13.5 V. The threshold voltage shifted ~ 6.5 V towards negative voltages when the bias was swept from -20 V to 20 V and ~2.5 V towards positive voltages in the opposite direction.



Figure 6.22 Capacitance versus voltage characteristics of the memory device at 1 kHz with bias scans from 0 to -20 V (0), -20 V to 20 V (n) and 20 V to <math>-20 V (p) applied to the Al electrode.

Finally, the hysteresis was absent when the voltage sweep range was reduced to -10 V to 10 V as seen in figure 6.23.

6.5.2.3 Discussion

It was deemed that the hysteresis observed in both current and capacitance versus voltage plots were due to the presence of the floating gate in the memory device. In the absence of this floating gate, the hysteresis is non-existent as seen in figure 6.19. Furthermore, from this figure, the effectiveness of the insulating properties of the PSQ layer can be examined.

Although the voltage ranges of each measurement were different, we are able to conclude that the presence of the PSQ layer between the ITO electrode and the P3HT layer significantly reduced the current flow. As expected the current density of the Schottky diode in both reverse and forward bias were much higher compared to the other devices. Interestingly, under positive voltage, the current in the MISM device is only partially controlled by the PSQ insulating layer. In the MISM device with an ideal insulating layer, the current should be totally controlled by the voltage drop across the insulator.



Figure 6.23 *C-V* characteristics of the memory device at 1 kHz when the voltage was swept from -10 V to 10 V.

When a sufficiently high positive voltage was applied to the ITO electrode, we believe that electrons from the depletion region at the PSQ/P3HT interface are injected into the PSQ. Therefore the current flow through the MISM device at positive voltages is higher than expected. Furthermore, the effective device area of the MISM device may be much larger than the top electrode due to lateral current

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flow in the P3HT film. Therefore, coupled with good electron injection properties of aluminium, more electrons can be injected under positive bias.



Figure 6.24 *Current-voltage characteristics for all devices studied in this chapter. The voltage polarity is that appearing at the ITO electrode.*

On the other hand, the observed current in the negative voltage region was found to be low. This may be due to the fact that holes accumulated at the PSQ/P3HT are blocked from being passed through the PSQ layer. Additionally, Al is generally not a good hole injector, thus the density of the holes at the interface would be insufficient to create a strong field across the insulator layer adequate for holes injection. Beside that, the formation of the depletion region at the Al/P3HT interface in negative voltage also reduced the current flow through the MISM device. From the currentvoltage characteristic of the MISM device (figure 6.24) it is suggested that under certain conditions, the PSQ film allows the flow of electrons but blocks the passage of holes.

As was expected, the current in the memory device when a positive voltage was applied to the ITO electrode was found to be considerably lower compared to other devices. The trapping of the electrons in the floating gate reduced the field across PSQ1, which therefore becomes current limiting. When the negative voltage was applied to the ITO electrode, it is thought that hysteresis occurs due to detrapping of electrons from the floating gate. At low negative voltage, electrons trapped in the floating gate keep the field across PSQ1 low, then at about -13 V, electrons start to be discharged and the field started to rise. Consequently, the current flow increased across the device. At high negative voltage, all the electrons in the floating gate have been discharged and as a result, a net hole charge is now trapped. Therefore, the field across PSQ 1 remains high and so is the current flow.

It is believed that the hysteresis found in the C-V plot (figure 6.22) of the memory device provides further support for the presence of electrons trapped in the insulator stack. This hysteresis is a well-known charge storage effect in the insulator especially in metal-ferroelectric-semiconductor-metal devices [22-32] and in the device with embedded nano-crystal in the gate insulator [33-45]. Since this effect

was not present in the MISM device, the charge storage is attributed to the presence of the thin Au layer embedded in the insulator layer of the memory device.

Figure 6.25 shows an energy diagram describing the storage and discharge of electrons in the floating gate memory device. This figure will be referred to from now onward. Figure 6.25 (a) shows the relative Fermi level of each metal used in fabricating the memory device. After the contact was made and in thermal equilibrium, all the Fermi levels of the metal were aligned (see figure 6.25 (b)), although there is a P3HT layer separating the second insulator from the Al electrode. When the voltage sweep was started at 0V to -20V to the aluminium electrode, the depletion region was created at the PSQ/P3HT interface. And as the applied voltage become more negative electrons were injected into and trapped in the floating gate for as long as the negative voltage increased (see figure 6.25 (c)).

Then when the voltage was swept from -20V to 0V, the electric field experienced by the electrons in the floating gate started to decrease and as a result some of the trapped electrons discharged to the P3HT (figure 6.25 (d)). However, most of the injected electrons were still stored in the floating gate, thus shifting the threshold voltage to a more negative value. On the other hand, when the voltage was swept from 0V to 20V, at first the majority carriers (holes) start to accumulate at the PSQ/P3HT interface. Therefore, at low positive voltage, trapped electrons in the floating gate reduce the field across PSQ1, limiting the current flow (figure 6.25 (e)).



Figure 6.25 Energy diagram illustrates the storing and discharging of the electrons in the floating gate of the memory device, I_1 and I_2 is the first and second insulator layers respectively. Sweeping voltages were applied to the aluminium electrode.

The increase in the electric field in PSQ2 coupled with the accumulation of positive charges at the interface leads to the discharge of the electron from the floating gate (see figure 6.25 (f)). As the voltage become more positive, all the electrons in the floating gate discharged. Since the floating gate might be in the form of an isolated island, the discharge of the electrons leaves a net positive charge on the gate. Therefore, at 20V there are a maximum number of positive charges trapped in the floating gate, and when the voltage becomes less positive (20 V to 0 V), some of the electrons from the P3HT layer recombine with holes in the floating gate. However, the remaining free holes in the floating gate shift the threshold voltage to a more positive value (see figure 6.25 (g)). From figure 6.22, the negative threshold voltage shift is ~ 5 V compare to ~ 2.5 V for the positive voltage shift. The source of holes which cause the positive threshold voltage shift is only limited to the positive charges left by the discharging of the electrons during the positive voltage sweep. On the other hand, the electrons can be injected from the depletion region at the PSQ/P3HT interface. From MISM dc characteristics, it is seen that only electrons can be injected through the PSQ insulator. The idea of trapped electrons and holes causing both a positive and negative threshold voltage shift respectively is consistent with the concept of the floating gate memory device discussed in chapter 3.

Furthermore, the constant low capacitance seen at negative voltages implies that the depletion region width at the PSQ/P3HT interface is constant which indicates that the P3HT layer is fully depleted. Assuming the measured capacitance when the device was driven into accumulation is equal to the insulator capacitance ($C_{in} = 297$ pF), when the depletion region capacitance, C_d , is estimated from figure 6.22 to be ~ 346 pF. The width of the depletion region is then calculated to be ~ 210 nm which is

close to the thickness of the P3HT layer estimated from the Schottky diode structure (see page 180, section 6.2.2). Additionally, the absence of a dispersion due to the depletion region at the Al/P3HT interface which should appear at positive voltages can again be explained by current leakage in the depletion region at this interface.

6.5.3 AC Characteristics of the Flash Memory Device

Measurements of the frequency dependence of the admittance were started at 0 V and then the applied voltage increased to positive voltages. The applied voltage was then returned to 0 V, before proceeding to the negative voltage. Figures 6.26 and 6.27 showed the capacitance-frequency and loss-frequency characteristics of the memory device for a wide range of applied voltages. The growth and collapse of a thin depletion region at the Al/P3HT contributes to a variation of the measured capacitance at low frequency when positive voltage was applied to the Al electrode. Under positive voltage, it is suggested that holes accumulate at the PSQ/P3HT interface; therefore the capacitance of the insulator stack dominates the measured capacitance. As seen from figure 6.26, the variation in the low-frequency capacitance under positive voltages was very small. On the other hand, when negative voltages were applied, a depletion region was created at the PSQ/P3HT interface. As the negative voltage increases, the depletion region increased and the measured capacitance decreased. Eventually the depletion region at the PSQ/P3HT interface dominates the measured capacitance (figure 6.26).

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Figure 6.26 Capacitance versus frequency characteristics of the memory device at different voltages applied to the Al electrode.

As seen from figure 6.26, 6.27, and 6.28, there were four possible dispersions occur in the flash memory device especially visible when the memory device was driven into an accumulation mode. The first dispersion (A) occurred at a frequency below \sim 1 kHz, the second dispersion (B) occurred between 1 kHz and 50 kHz, the third dispersion (C) occurred between 100 kHz and 1 MHz, and the fourth dispersion (D) occurred at a frequency above 1MHz. The first three dispersions are visible in the loss versus frequency plot (figure 6.27), while the fourth dispersion can be seen only in the complex admittance (Cole-Cole) plot (figure 6.28) because the measurement range is only between 20 Hz and 1 MHz.



Figure 6.27 Loss versus frequency characteristics of the memory device at different voltages.

In addition, these four dispersions were highlighted in figure 6.29 when the complex admittance of the memory device at 20 V, -1 V and -20 V were replotted. Upon applying negative voltages to the Al electrode, followed by a positive voltage, at 20 V, the main visible processes are due to depletion region dispersion at the Al/P3HT and PSQ/P3HT interfaces (B), electron-hole exchange between the floating gate and the semiconductor (C) and lateral current (D). The dispersion arising from the contact resistance (A) only became visible when the other dominant processes were suppressed (see figure 6.29). At low negative voltages, for example -1 V, the magnitude of processes B, C, and D started to decrease while process A started to appear. Finally, when -20 V was applied, only the processes due to contact resistance and lateral current remained. Interestingly, the size of the arc D remains the same when negative voltages were applied to the Al electrode. All these processes were also seen in the MISM device except process C.

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Figure 6.28 Complex admittance (Cole-Cole) plot of the memory device under different voltages applied to the Al electrode.

Furthermore, the shape of the plot of process D should be a straight line if this process is associated with a dc loss. However, as seen in figure 6.29, instead of a straight line, process D is represented by a curve indicating that another possible dispersion occurs at low frequency. The equivalent circuit in figure 6.30 is used to understand how such a loss process could arise from lateral current flow through the semiconductor layer. This lateral current changes the effective area of the insulator outside the contact area and is represented by additional series of RC elements. At lower frequencies more and more of these elements contribute to the measured signal and as a result, the measured capacitance increases as observed in figure 6.16.



Figure 6.29 Different processes occur in the memory device arising from (A) contact resistance, (B) depletion dispersion, (C) electron-hole recombination, (D) lateral current through P3HT residue surrounding the top electrode.

Because the bridge measures admittance, the response of a series RC circuit will lead to a dispersion as can be seen from transforming the impedance

$$Z = R - \frac{j}{\omega C}$$

to its corresponding admittance

$$Y = \frac{R\omega^2 C^2 + j\omega C}{1 + \omega^2 C^2 R^2}.$$

In the MISM device, the P3HT surrounding the top electrode was not removed, whereas in the memory device the P3HT surrounding the top electrode was removed as indicated by yellow area in figure 6.30. As a result, the effective area for the lateral current flow in the MISM device is very high but in the memory device is much lower. The complex admittance plot of the MISM device in figure 6.31 shows the exceptionally high lateral current effect as compared to figure 6.29 for the memory device where the dispersion is clearly seen.



Figure 6.30 Equivalent circuit of the MISM and memory device showing how the lateral current changes the area of insulator outside that defined by the aluminium electrode. PSQ here indicates PSQ/Au/PSQ layers in the memory device and only PSQ layer in MISM device. The vertical broken line indicates the area of an ideal device without additional RC elements and the yellow area indicates the effective area of the memory device when P3HT surrounding top electrode was removed.



Figure 6.31 Complex admittance plots of the MISM device showing the arcs due to (A) contact resistance, (B) depletion dispersion and (D) lateral current. Note the voltage for MISM device was applied to the ITO electrode.

Furthermore, from the dispersion at the frequency between 50 kHz and 1 MHz (arising from the Maxwell-Wagner effect), the components of the equivalent circuit in figure 3.31 were estimated and tabulated in table 6.6. When positive voltages were applied to the Al electrode, a depletion region is created at the Al/P3HT interface. However, as shown in table 6.6, this depletion region was totally collapsed when the applied voltage exceeded 5 V. Therefore, the maximum depletion layer thickness at the Al/P3HT interface was estimated to be ~6 nm.

On the other hand, when negative voltage was applied to the Al electrode, the depletion region was created at the PSQ/P3HT interface and as seen in table 6.6, this

depletion region grows at a very fast rate between 0 V to 5 V. As the negative voltage increases to more than -10 V, the depletion region grows very slowly due to the electrons in the floating gate attracting holes to the interface and so making it harder to deplete. As a result, the P3HT layer was not fully depleted even at high voltages.

Table 6.6 The depletion region capacitance and thickness of the memory deviceunder different applied voltages deduced from semicircle (B) in figure 6.29.

Applied voltage (V)	C _{LF} (pF)	C _d (pF)	Depletion width (nm)
20 to 5	288	∞	0
1	281	11561	6.2
0	281	11561	6.2
-1	272	4896	14.7
-0.5	253	2081	34.6
-1.5	229	1118	64.5
-2	216	864	83.4
-3	198	634	113.7
-4	190	558	129.1
-5	183	502	143.6
-10	180	480	150.1
-20	177	459	157

Additionally, the Cole-Cole plot of the memory device provides us with information about the capacitance of the insulator stack, which in this case is ~280 pF at 0V. This

value is lower than the low frequency capacitance shown in figure 6.26. Therefore, it is suggested that the capacitance of 350 pF is the measured capacitance of the insulator stack with the presence of the trap in the insulator. This high capacitance value can be explained by assuming that the gold floating gate consists of a continuous layer over the whole device area. Therefore the injected electrons charge the whole of the gold at low frequency giving a bigger effective area.

6.6 Summary

A flash memory device has been fabricated successfully. Hysteresis was clearly observed in both I-V and C-V characteristics of the device. The hysteresis was only observed if the sweep voltage range was large enough. The hysteresis is attributed to the trapping and detrapping of charges in the floating gate embedded in the PSQ layers.

The admittance data supports our suggestion that the hysteresis observed in the I-V and C-V plots is due to charge storage in the floating gate. When a negative voltage was applied to the aluminium electrode, holes accumulate at the PSQ/P3HT interface. At the same time, a small depletion region was also created at the Al/P3HT interface. On the other hand, when positive voltage was applied, a depletion region was created at the P3HT/PSQ interface.

The Cole-Cole plot reveals that four relaxation processes occur in the flash memory device. These processes are attributed to the following mechanisms (a) lateral current

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flow through the P3HT film surrounding the top electrode (b) hole-electron recombination (c) collapse/growth of the depletion region and (d) contact resistance effect.

Hysteresis was absent in both the I-V and C-V plots of the MISM device. However, we observed rectification in the I-V characteristic with forward bias when positive voltage was applied to the ITO electrode. High currents in the forward bias can be explained by the injection of electrons from the depletion region at the PSQ/P3HT interface into the PSQ layer all the way to the ITO electrode. The admittance data showed only dispersion due to the collapse/growth of the depletion region. The relaxation frequency is lower when negative voltage was applied to the ITO electrode compared to the positive voltage. Additionally, the relaxation frequency increased when the positive voltage increases. Finally, from the complex admittance plot it is seen that the process due to the hole-electron recombination is absent and the maximum depletion width at the Al/P3HT interface is much smaller than depletion region at PSQ/P3HT interface.

As expected, the current flow through the PSQ insulator is considerably lower, however, the current flow is temperature dependent. The activation energy is dependent on applied voltage consistent with the Schottky conduction model. PSQ bulk resistivity at room temperature is comparable to that of thermally grown amorphous SiO₂. Furthermore, the capacitance of the PSQ insulator is independent of temperature and the applied voltage.

Finally, it is also shown that the I-V characteristic of the P3HT diode displayed a higher rectification ratio compared to the MISM device. From the admittance data, a depletion region is seen to be created at the Al/P3HT contact and the P3HT layer is almost fully depleted when -2 V is applied to the ITO electrode. Moreover, the circuit relaxation time was estimated to be ~ 10 ms and from the Mott-Schottky plot, the acceptor doping density in the P3HT was estimated to be 1.1×10^{-16} cm⁻³.

6.7 References

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7.1 Background

The initial aim of this study was to investigate the origin of the previously reported memory effect in PCDM diode. After demonstrating the sensitivity of the effect on growth condition, the focus of the study was changed to the fabrication of a polymer flash memory.

The theoretical framework of organic semiconductor and device theory was reviewed to help our understanding of the memory effect in polymer devices. Different types of possible candidates for organic semiconducting materials have been covered with special attention being paid to the polymers used in this study, i.e. P3HT and PCDM. Charge transport in semiconducting polymers has been explained in terms of polarons, bipolarons and solitons. The metal-semiconductor contact also has been discussed with an explanation of blocking and ohmic contacts together with a review of conduction mechanisms across the interface and in the bulk. Charge transport in disordered organic semiconductors has been discussed in particular the Bässler model.

Basic device concepts including the Schottky diode and the MIS device have been discussed. The Schottky diode was modelled by an equivalent circuit consisting of two RC circuit elements in parallel. These elements represented the bulk and depletion layer and yielded a single dispersion in the theoretical admittance-frequency plot. The presence of a contact resistance required modification of the model to include a small series resistance which caused the appearance of a second dispersion at high frequency. The MIS device in accumulation and depletion modes

was modelled in a similar manner. Different types of memory device have been reviewed including the floating gate, nano-crystal and ferroelectric material memory device. Finally, to help our understanding of the memory effect in polymer devices, progress in the development of polymer memory device has been reviewed.

From this review, we found that the memory effect observed in the PCDM diode [1] still very much unclear. Therefore in this thesis, a systematic study has been conducted in the first part of the thesis to understand the memory effect in such device. Additionally, little work has been done to develop the organic equivalent of flash memory device. Thus, in the second part of the thesis, a thin layer of gold was embedded in an insulator to fabricate an organic flash memory diode.

7.2 PCDM Diode

Generally, the quality of the PCDM film was good. From AFM analysis, the surface of PCDM was shown to be acceptably smooth for film thickness in the range 200 - 300 nm. PCDM diodes fabricated from a freshly prepared CDM monomer solution showed a very good memory effect; in fact the memory ratio of this device was ~10 times higher than the previously reported value for PCDM diodes by Mills and co-workers [1]. Although, the DC characteristic of the PCDM diode displayed little or no rectification, the current of this device was found to depend on the direction of the voltage sweep especially at low voltage. Starting at +5 V, a 'high' conductance state was observed while a 'low' conductance state was displayed when the voltage sweep started at -5 V. This hysteresis was explained as being due to space charges arising

from the migration of the ionised acceptor (BF_4^-). When negative voltage was applied to the Al electrode, BF_4^- ions were repelled from that interface thus causing the depletion region to grow wider than expected. As a result, the device was driven into a 'high' impedance state. On the other hand, when positive voltage was applied to the Al electrode, BF_4^- ions were attracted to the interface which caused the depletion region to grow thinner than expected and consequently, the device was driven into a 'low' impedance state. However, it was shown that, when four devices were produced successively from the same solution the I-V characteristics showed two main changes: (a) a reduction in the magnitude of the memory effect and (b) a general decrease in the observed currents.

Changes in the electrical characteristics of the PCDM diode were consistent with other measurements. The UV/Vis spectrum showed the presence of polaron or bipolaron bands in the first two PCDM films. These bands arose from the p-doping of the films by the dopant, BF_4^- . This dopant was absent or compensated by the counter-cations in the later films explaining the diminished memory effect. The compensation of the dopant was supported by FTIR spectroscopy. It was found that quaternary ammonium counter-cations become trapped in the later films. Therefore it was concluded that BF_4^- played a major role in the memory effect in the PCDM diode, a conclusion which is further supported by the extension of the dispersion in the admittance plot. This extension was attributed to the slower ionic diffusion in the bulk of the polymer.

The formation of depletion regions at both the Al/PCDM and ITO/PCDM interfaces has been shown both from surface potential measurements and the C-V plot. This explains the absence of the expected rectification in the I-V characteristics of the PCDM diode. Additionally, the maximum capacitance in the low frequency region also decreased in the later film which is consistent with an increase of the depletion region in these films.

Finally, it is concluded that PCDM diode did show a very good memory effect provided that PCDM film was electrodeposited from a freshly prepared monomer solution. In such film, no over-oxidation of the thiophene ring was occurred and the film was moderately doped with the BF_4^- anions (quaternary ammonium counter cations should be absent in the film or otherwise its will compensate the anions effect).

7.3 Flash Memory Device

The organic semiconductor used in this thesis was studied to determine the DC and AC behaviour of a typical P3HT diode. From the I-V plot, it has been observed that the ITO/P3HT/A1 diode displayed very good Schottky diode behaviour with rectification ratios of ~10⁴ at ±1 V and ~10⁶ at ±2 V. Additionally, it has also been shown that this device was fully depleted at -2 V and possessed a single relaxation frequency with τ_R =1.1 x 10⁻⁵ s. From Mott-Schottky analysis, it was found that the acceptor doping density, N_A , of the P3HT film used in this study was 1.1 x 10¹⁶ cm⁻³.

The currents flowing through the PSQ insulator is very low but thermally activated. The activation energy in the temperature range 25°C to 60°C was between 0.27 eV and 0.41 eV and 0.88 eV to 1 eV in the temperature range 70°C to 130°C. The activation energy was dependent on the applied voltage which is consistent with the Schottky conduction model. However, the dielectric constant extracted from the ln J Vs V^{1/2} plot was too high compared to the value from the literature and was inconsistent with the changes in the measured capacitance. PSQ bulk resistivity at room temperature is ~9.5 x 10¹⁵ Ω cm under an electric field of 1 MV/m. Furthermore, the capacitance of the PSQ insulator is independent of temperature as well as the applied voltage.

A rectification ratio of 10^3 was found in the I-V characteristic of the MISM device with a current density of 1.12×10^{-2} A/m². The reverse current in the MISM device was comparable to that in the MIM, while the forward current was between those in the Schottky diode and the MIM device. High forward currents in the MISM device has been attributed to the injection of electrons from the depletion region at the P3HT/PSQ interface into and through the PSQ film. From the admittance results, it has been shown that, besides the main depletion region at the P3HT/PSQ interface (maximum thickness ~260 nm); a much thinner depletion region was also created at the Al/P3HT interface (maximum thickness ~40 nm) during the negative voltage sweep. Finally, it has also been shown that the relaxation frequency of the MISM device was voltage dependent. In the accumulation mode, the relaxation frequency was found to be ~60 kHz but shifted from ~80 kHz to ~120 kHz as the depletion region grew in depletion mode. It has been demonstrated that a memory effect can be induced in a polymer MIS capacitor by embedding a thin layer of gold in the insulator. Hysteresis in the I-V and C-V plots has been observed as seen in figure 6.5.1 and 6.5.3. The hysteresis started to emerge when the voltage sweep range was greater than -10 V to 10 V. From C-V plot the threshold voltage was seen to shift by ~7.5 V in opposite sweep directions. The mechanisms of the memory effect observed in this device were explained graphically in figure 6.5.6. When negative voltage was applied to the ITO electrode, a depletion region was created at the P3HT/PSQ2 interface and if the voltage was sufficiently high, some of the electrons from the depletion region will be injected into the floating gate through the PSQ2 layer. Therefore, when the voltage was swept from negative to positive values, the threshold voltage will be shifted to the negative value. On the other hand, when positive voltage was applied to the ITO electrode, the holes will be accumulated at the P3HT/PSQ2 interfaces and a small depletion region was also created at the Al/P3HT interface. The accumulation of the holes discharges the electrons in the floating gate and if the applied positive voltage was sufficiently high, net positive charge was created in the floating gate as a result of the extra electrons being discharged. Consequently, the threshold voltage was shifted to a positive value.

The Cole-Cole plots in figure 6.5.8 reveal the presence of four possible processes in the flash memory device. The first process occurs at low frequency and is due to the lateral current flow through the residual P3HT surrounding the top electrode. The second process between 1 kHz and 50 kHz was due to hole-electron exchange between the floating gate and the semiconductor. The third process between 100 kHz and 1 MHz was due to the collapse/growth of the depletion region, and finally, the process at high frequency was due to the contact resistance.

Finally, the hysteresis observed in the organic flash memory device was absent in the MISM device which enable us to conclude that the gold floating gate in the insulator plays a major role in the memory effect in this device.

7.4 Future Work

Since PCDM diodes prepared from fresh monomer solution have shown a good memory effect, finding another deposition technique or modification of the electrodeposition technique is vital if we are going to fabricate organic memory devices from this material. The electrodeposition technique currently being used to produce PCDM films makes it difficult to control the composition of the monomer solution such as dopants (electrolytes) and monomer. Therefore, modification of the electrodeposition technique by allowing the monomers and the electrolytes to be replenished and the waste to be drained and treated (electrochemically taking out the quaternary ammonium counter-cations from the solution), could lead to better control over the composition of the monomer solution. Other than that, finding any solvent that can dissolve the PCDM film might permit the use of simpler fabrication techniques such as spin-coating.

Although significant progress has been made in fabricating a flash memory device, further work is necessary to optimise the structure. In the current device, an aluminium contact was made to the device to provide a current limiting mechanism the depletion region at the Al/P3HT interface – when the electrode is biased positively. Therefore, it is important to validate this assumption by replacing aluminium with a hole injector such as gold where no such limitation will occur. If the aluminium contact did limit hole injection into the semiconductor, this new device should show high currents possibly without any rectification in the MISM device and the memory effect in the floating gate device should be bigger. Furthermore, the final step in producing the flash memory device is to make a metalinsulator-semiconductor field effect transistor (MISFET) and use the source-drain current to sense the charge on the floating gate. Therefore, since the source and drain will be formed in gold, it is important to know that the memory can be induced with a gold rather than aluminium contacting the P3HT.

Other information required for fully characterising the flash memory device includes the following;

- (i) Holding time of the charges after the power is turned-off.
- (ii) The frequency dependence of the capacitance and loss of the memory device when the applied voltages were varied from negative to positive and returned to negative again and repeated for a few times. The capacitance and loss versus frequency curves were expected to follow the C-V plot; whereby when the voltage was varied from negative to positive, the low frequency capacitance starts to increase at -10V and drastically increase to the maximum value at ~ -5 V. Then the capacitance will slightly increase before reaching a constant value above ~0V. On the other hand, the low frequency capacitance was expected to decrease at ~ 5V when the voltage was varied

from positive to negative. The capacitance should drastically decrease below 5 V and reach a minimum value at \sim -5V. The value of the capacitance at 0V should be much higher when the voltage was varied from negative to positive compared to the opposite direction.

- (iii) The effect on the C-V plot if the measurements were repeated for a few cycles while varying the voltage sweep ranges. This work will enable us to determine the exact turn-on voltage of our device and study the reliability of the hysteresis observed in this thesis.
- (iv) Long term measurements were also very useful to determine the device lifetime as well as the number of switching events that the device can undergo.

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Observations on the memory effect in diodes fabricated from carbon-bridged dithiophenes

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Abstract

A number of laboratories including our own have reported hysteresis, i.e. a memory effect, in the current–voltage characteristics of semiconducting polymers. Here we report further results on the hysteresis observed in electropolymerised films of a carbon-bridged dithiophene. In particular, we present spectroscopic evidence that shows the effect requires a high degree of conjugation and moderate doping of the polymer. The presence of mobile ions per se in the film is insufficient to cause the effect. Successive film samples produced from the same monomer solution show progressive changes in both the UV and FT-IR spectra consistent with reduced conjugation in the polymer coupled with reduced doping by the BF_4^- counterions. These changes correlate with a reduction in hysteresis and a general lowering of film conductivity. From the spectroscopic evidence we develop a possible band energy scheme which suggests that both aluminium and ITO should make rectifying contacts to the polymer thus confirming our earlier findings.

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Keywords: Semiconducting polymers; Electropolymerization; Electronic memory; Polymer electronics; Diodes; Optical spectra

1. Introduction

Recent years have seen a rapid increase in the use of semiconducting polymer materials in electronic devices. The interest has arisen from the ability presented by these materials to combine the control of polymer structure with relatively economical routes to polymer synthesis and subsequent processing to achieve desired electronic, optical, chemical and mechanical properties. Most attention has concentrated on organic light emitting diodes (OLEDs) [1] and field effect transistors (FETs) [2]. However, a number of laboratories have investigated the possibility of fabricating organic memory devices [3-8] with several focusing attention on a reversible, switching effect that is present in some organic diodes [4-8]. If stable and long-lived, such an effect may find application in non-volatile memories although Scott has argued that devices based on this effect may be impractical [9]. Nevertheless, studying such effects in diodes is worthwhile since it increases our understanding of charge injection and transport as well as of ionic migration in such structures.

* Corresponding author. E-mail address: martin@informatics.bangor.ac.uk (D.M. Taylor). The intriguing properties and potential of electroactive polymers based on the cyclopentadithiophene skeleton were highlighted recently by Coppo and Turner [10]. Yonezawa et al. [11] have suggested that conjugation between heterocyclic rings is better in these materials than in oligomers so that they should be characterised by lower HOMO–LUMO (π – π^*) bandgaps. Indeed, the derivative incorporating the dicyanomethylene moiety linked to the bridging carbon atom has received considerable interest following reports that polymer films produced by electrodeposition exhibited a low bandgap [12].

Reversible switching in diodes fabricated from the resulting polymer, poly(4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4b']dithiophene) (PCPDT), was first reported by Taylor and co-workers [4,5]. They argued that the effect arose from the presence of a narrow depletion region at the polymer/indium tin oxide (ITO) interface formed by ionised dopant ions. The switching effect was then seen to be a consequence of increased or decreased charge injection into the device resulting from a voltage-induced change in the concentration of dopant ions in the vicinity of the electrode. A similar explanation was given by Majumder et al. [7] for switching in diodes formed from poly(3-(6-methoxyhexyl)thiophene). By controlled doping of the semiconducting polymer poly(3-hexylthiophene), Smits et

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[8] confirmed the feasibility of developing this concept into functioning non-volatile memory. In a novel, bilayer device ported by Ma et al. [13], the memory function was believed arise from the field-induced migration of Cu^+ ions from the ode into the organic film.

In our earlier work it was observed, though not reported, that e magnitude of the memory effect was variable from device device. In particular, the effect diminished during the batch oduction of films from the same monomer solution suggesting at close control of electropolymerisation conditions would be cessary in any continuous process used for producing these vices. In order to understand the reasons for this, we have dertaken a spectroscopic investigation of the deposited films, e results of which have provided a possible explanation for s observation. In summary, the reduction in memory effect flects changes in the chemistry of the deposited polymer when ectrochemical conditions change during the batch production films as monomer and dopant ions are consumed.

Experimental

Sample fabrication has been described fully in our preous publications [4,5]. Briefly, films of PCPDT were ectrodeposited from a degassed solution of the monomer -dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b']dithiophene) solved in nitrobenzene to which tetrabutylammonium rafluoroborate was added as a supporting salt. The film was own onto a precleaned, ITO-coated glass slide at an electrode tential of 1.6 V (versus Ag) following a short nucleation step 2.0 V. When the film had reached the desired thickness, the bstrate was removed to a monomer-free bath for dedoping a potential of 0.0 V (versus Ag) by extracting tetrafluorobate anions (BF₄⁻) until the measured current had fallen to $20 \,\mu\text{A/cm}^2$ (or less) for 300 s. This dedoped film was then noved from the cell, washed in acetone and dried in a stream dry nitrogen. The original monomer solution was then used to ow three further films in succession following the procedure tlined above. These batches of four samples were then stored under vacuum until required. Test devices were completed by evaporating circular aluminium contacts 2.54 mm^2 in area and ~300 nm thick onto the film in a turbopumped vacuum system. The thickness of the polymer films was determined by scoring with a sharp blade and measuring the depth of the score using an AFM.

For the electrical measurements, the devices were placed in a sample holder in a chamber evacuated to $<10^{-5}$ Torr. The dc characteristics were obtained using an automated *I–V* plotter (HP model 4140B) incrementing the voltage applied to the ITO electrode in steps of 0.1 V every 5 min to eliminate displacement current effects [4,7]. Small-signal ac admittance measurements over the range 20 Hz to 1 MHz were made with an LCR Meter (HP model 4284) with a test signal of 50 mV. Optical absorption spectra were obtained in transmission using a UV–visible spectrometer (Hitachi model U2000). Fourier transform infrared (FT-IR) spectra were also obtained in transmission using a Bomem model MB-100 spectrometer.

3. Results

3.1. Electrical properties

Fig. 1 shows the extremes of behaviour observed in the current-voltage characteristic of the diodes fabricated from the different films. The double-log plots in Fig. 1(a) are typical of diodes D1 fabricated from the first film produced with fresh monomer solution in the electrolytic bath. When sweeping from +5 to 0 V and then to -5 V, (two upper plots) the currents are high. This contrasts with the much lower currents seen on the reverse sweep from -5 to 0 V and then from 0 to +5 V (twolower curves). The resulting hysteresis (the so-called memory effect) is consistent with our earlier results [4,5] but much larger. The difference between the positive and negative voltage sweeps is now almost two orders of magnitude and the currents are generally much higher.

Fig. 1(b) typifies diodes D4 formed in films grown during the 4th cycle using the same monomer solution. As can



. 1. Double log plots of the current-voltage characteristics for diodes D1 (a) and D4 (b). The upper two plots in (a) are for the voltage sweeps from +5 to 0 V and m 0 to -5 V applied to the ITO electrode. The lower two plots are for the reverse sweep and clearly demonstrate a high degree of hysteresis.

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Fig. 2. Frequency-dependence of the capacitance, C, of diodes D1 (\Diamond) and D4 (\Box) plotted together with the measured loss, G/ω (conductance/angular frequency) in diodes D1 (\times) and D4 (+).

be seen, there is no hysteresis and the currents are generally lower.

The small-signal admittance of our diodes is defined as $Y = G + j\omega C$ where G is the conductance, C the capacitance and ω is the angular frequency. In Fig. 2 are shown the capacitance, C, and loss, G/ω , of diode D1 which again is similar to that presented earlier [5], i.e. one main dispersion ~200 Hz which was ascribed to the presence of a depletion region at one or both electrodes. For diode D4 the main dispersion has shifted to frequencies well below the measurement range, consistent with the reduction in bulk conductivity. For diodes formed in films grown during the second and third cycles, the behaviour was intermediate between these two extremes.

3.2. Spectral characterisation

The UV-visible spectra of PCPDT films used for fabricating diodes D1 to D4 are shown in Fig. 3. Three main electronic transitions can be identified. These are centred close to 350, 500 and 900 nm. Consistent with the changes observed in the electrical measurements, changes are also seen in the UV-visible spectra: the bands at 500 nm (2.5 eV) and 900 nm (1.4 eV) decrease in intensity from D1 to D4 while that at 350 nm (3.6 eV) increases.

The main feature in the FT-IR spectra of all the films (Fig. 4) is the strong background absorption arising from electronic



Fig. 3. UV-visible spectra of electrodeposited polymer films used to fabricate liodes D1–D4. The spectra have been shifted vertically for clarity.



Fig. 4. FT-IR spectra of polymer films electro-deposited successively from the same monomer solution and used to fabricate diodes D1–D4.

transitions which has also been observed during the p-doping of related materials [14–17]. The onset of such transitions, at around 1500 cm^{-1} (0.19 eV), has been attributed to transitions from the valence band (HOMO level) to the lowest lying polaron level and also to transitions between polaron bands but with little clear evidence to support the one in preference to the other. We see again in these samples progressive changes in the spectra with transmittance increasing from D1 to D4 suggesting a decrease in the degree of p-doping in the film. In our previous work [14], and in that of others [15–17], high pdoping enhanced the intensity of many of the vibrational bands in this spectral range. This is clearly the case here also, with the so-called infrared active vibrations (IRAVs) corresponding well with Raman spectra of PCPDT [18] obtained during spectroelectrochemical measurements (see Table 1). In their study,

Table 1

Comparison of the main FT-IR absorption bands of PCPDT films prepared in this study with the Raman spectra reported by Huang and Pickup [18]

Vibration	Wavenumber (cm ⁻¹)	
	Raman	FT-IR
С _в -н	3171	3084
Alkyl C-H	2900-3000ª	2850-3000 ^b
C≡N	2230	2228
	2217 ^c	2203 ^b
C _B =O	1712°	
$C = C(CN)_2$	1589	1587
$C_{\alpha} = C_{\beta}$	1511	1520
C _B -C _B	1345	1344
=C-CN	1334	
C _B -OH	1256°	
C _B -C=	1225	1220
Inter-ring $C_{\alpha} - C_{\alpha'}$	1161	1178
C–S–C	702	
	782	770

The Raman spectrum of the neutral polymer was obtained in situ in an electrochemical cell containing acetonitrile and Bu_4NPF_6 . That of the oxygen-modified polymer was obtained ex situ.

^a Only observed in the in situ measurement.

^b Vibrations observed only in films used to fabricate diodes D2-D4.

^c Vibrations observed only in oxygen-modified polymer film.

+ Model

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ang and Pickup [18] also reacted their polymer with oxygen nich resulted in the appearance of new bands at 1712 cm^{-1} $_{\beta}=O$) and 1256 cm^{-1} (C_{β}-OH). It could be argued that the ong band at 1717 cm^{-1} in our FT-IR spectra provides evince for the oxidation of carbon at the β site in our films also. at this occurred, though, we should expect to see significant takening of the band corresponding to the aryl C-H stretch at 84 cm⁻¹ and also of the =C-CN band at 1344 cm^{-1} , coupled th a splitting of the CN stretch band at 2228 cm^{-1} . None of ese features are seen in diode D1. Furthermore, the inter-ring $_{c}-C_{\alpha'}$ vibration at 1178 cm^{-1} remains strong in this film, again ggesting that the ring structure has not been compromised by idation.

The FT-IR spectra of diodes D2–D4, however, show progres-'e increases in the alkyl CH stretch bands between 2850 and 00 cm^{-1} . Also seen is a reduction in the relative magnitude of e aryl CH stretch at 3084 cm⁻¹ and of the CN stretching vibran at 2228 cm⁻¹ as it splits to form a new band at 2203 cm⁻¹. ken together, these last changes provide some support for idation of the polymer. A possible mechanism suggested by ang and Pickup [18] is that –OH has been substituted at some ter C_β sites; the splitting of the CN stretch vibration then sugsts that the enol-OH group is hydrogen-bonded with some of \mathfrak{t} –CN groups. However, in the oxidised films produced by see authors this interpretation was further corroborated by the esence of an –OH band at 2759 cm⁻¹ which is absent in our ns.

Discussion

From the I-V plots in Fig. 1 it is clear that hysteresis is a charieristic of the first few films deposited from the same monomer lution and disappears by the fourth film. In Fig. 4, a reducn is seen in the background absorption in the FT-IR spectra successive batches of film. This indicates a reduction in the ensity of electronic transitions coupled with a shift to higher ergy. Such behaviour is consistent with reduced p-doping in : films and would also explain the reduction in the UV-visible sorption band centred at 900 nm (1.4 eV) which we have prevuly attributed to sub-bandgap transitions between polaronic rels.

The reduction in p-doping in successive films is also accomnied by changes in the vibrational bands, the most significant ing: the reduction in the aryl CH stretch band, the splitting the CN stretching vibration and the growth of the alkyl CH etch bands. The first two changes are consistent with hydroxtion of the outer C_{β} atoms of the thiophene rings as suggested Huang and Pickup [18]. Such a modification is expected to luce the conjugation in the ring structure and hence reduce conductivity of the film, as seen in Figs. 1 and 2. Reduced njugation is likely also to be the origin of the reduction in 500 nm band relative to that at 350 nm in the UV-visible ectra in Fig. 3. We believe that the former band represents the rinsic bandgap of the polymer ($\sim 2.5 \text{ eV}$), despite the molecr modelling calculations by Salzner [19] which estimate the)MO-LUMO gap in the monomer to be 3.23 eV reducing 1.72 eV in the polymer. While some discrepancy between



Fig. 5. A suggested band structure for the PCPDT polymer.

theoretical calculations and experimental data can be expected, nevertheless, the qualitative trends seen when modelling a series of oligomers and extrapolating to the polymer should be valid. One interesting such observation by Salzner is that the conduction band in PCPDT, which arises from a combination of thiophene LUMO states and the dicyanomethylene group, is believed to be narrow (calculated to be ~0.2 eV) owing to localisation of electrons around the latter group. On the other hand, the valence band, which arises from the HOMO states of thiophene, is wide (~2.4 eV).

Combining this information with that obtained from the electronic transitions observed in the FT-IR and UV-visible spectra, we may deduce a schematic band diagram for the first film to be deposited in any batch. In this scheme (see Fig. 5), transitions from HOMO to LUMO give rise to the UV-visible absorption centred at 500 nm. The broad absorption band centred at 900 nm arises from transitions between polaron states P1 and P2 which are assumed symmetrically distributed around mid-gap. The threshold at ~0.19 eV seen in the background absorption in the FT-IR spectrum corresponds to electronic transitions between the valence band (HOMO) and the polaron band P1.

XPS measurements on our films suggest that the valence band edge lies approximately 0.2 eV above the Fermi level of a clean platinum surface which has a work function, $\phi_W = 5.65 \text{ eV}$ [20]. This places the Fermi levels of aluminium, $\phi_W = 4.3 \text{ eV}$, and ITO, $\phi_W = 4.2-4.7 \text{ eV}$, slightly above the middle of the polymer bandgap. For moderate p-doping, the Fermi level of the polymer is expected to be close to the polaron band P1 in which case both electrodes are expected to form Schottky contacts to the polymer as suggested in our previous reports [4,5].

In films produced subsequently from the same solution, hydroxylation is not expected to give rise to the relatively strong alkyl-CH stretch vibration in the FT-IR spectra (see D3 and D4 produced in this particular batch). Rather this indicates the presence of tetrabutylammonium (NBu₄⁺) cations trapped in the film. These positively charged ions will neutralise the BF_4^- ions thus reducing their ability to dope the polymer, thereby providing an additional mechanism for decreasing film conductivity.

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5. Conclusions

References

We have shown that the memory effect in diodes formed from electrodeposited PCPDT films is a characteristic of films deposited from a freshly prepared electrolytic solution. The resulting polymer has an intrinsic bandgap of $\sim 2.5 \text{ eV}$ and, despite the dedoping step employed, contains sufficient residual dopant to form polaron bands which give rise to electronic transitions in the range $\sim 0.2-1.5 \text{ eV}$.

Preparation of successive batches of film from the same monomer solution leads to a decrease in the intensities of these lower energy transitions. The effect is associated with reduced conjugation and the trapping of significant concentrations of NBu_4^+ cations which neutralise the doping effect of the BF_4^- anion. Both mechanisms will lead to a reduction in film conductance.

The results suggest, therefore, that the memory effect in PCPDT does not arise simply from the presence of mobile ions, although their presence is a pre-requisite. The degree of conjugation and doping is also important.

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