A Molecularly Switchable Polymer-Based Diode

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Abstract:

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My own contribution to this development, originating from an idea first put forward by my tutor, Professor Magnus Berggren, is a design for a switchable polymer-based diode. Its architecture is based on a modified version of a recently developed highly-rectifying diode, where an intermediate molecular layer has been incorporated in the bottom contact. Due to its unique ability to switch its internal resistance during operation, this thin layer can be used to shift the amount of (forward) current induced into the rectifying structure of the device, and by doing so shift its electrical characteristics between an insulating and a rectifying behaviour (as illustrated bellow). Such a component should be of great commercial interest in display technologies since it would, at least hypothetically, be able to replace the transistors presently used to address the individual matrix elements.

However, although fairly simple in theory, it proved to be quite the challenge to fabricate the device structure. Machinery errors and contact problems aside, several process routes needed to be evaluated and only a small fraction of the batches were successful. In fact, it was not until the very last day that I detected the first indications that the concept might actually work. Hence, several modifications might still be necessary to undertake in order to get the device to work properly.

Nyckelord:
Conjugated polymers, metal/polymer-junctions, organic electronics, switchable diodes, molecular electronics.
to Michelle
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The (a) equivalent circuit of a switchable diode and its (b) principle electrical characteristics.
There are a number of persons who I would like to thank for their different contributions to the work presented in this text. First of all I would like to express my sincere gratitude to Professor Magnus Berggren, my tutor, for giving me the opportunity to work in the exciting field of organic electronics, and generously sharing his ideas. Additionally, lecturer Mats Fahlman, my examinator, is acknowledged for reviewing and excellently comment previous versions of my report, Anurak Sawatdee and Jessica Jonsson for experimental tutorage, and all members of the Organic Electronics group at Linköping University and ACREO AB for the friendly atmosphere I have experienced. Finally, special thanks is also due to my friends and family for their patience and understanding, and to my girlfriend Anna for time I have spent at work instead of with her.

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General Introduction

1.1 Background

The emergence of the field of conjugated polymers came about in the early seventies, when a researcher at the Tokyo Institute of Technology accidentally discovered a new way to synthesise trans-polyacetylene, producing free-standing silvery films instead of the usual dark powder. In 1977, inspired by its metallic appearance, Heeger, MacDiarmid and Shirakawa, then at the University of Pennsylvania, begun to expose such free-standing films of trans-polyacetylene to iodine and AsF$_5$, and found increases in conductivity of up to nine orders of magnitude. Thus, a new era in the field of polymers was born.

Early on, most of the research effort was concentrated on improving the conducting properties of the doped, i.e. oxidised, conjugated polymers. In some cases a conductivity comparable to that of single crystal copper, i.e. $10^5$ S/cm, have been found in doped trans-polyacetylene. With these new ‘synthetic metals’, scientists hoped to replace existing conducting materials with lightweight plastic electrical conductors, but due to poor environmental stability of the doped conjugated polymers, such applications have not yet been realised.

Instead, during the second half of the eighties, interest began to shift towards the pristine, semiconducting state of the conjugated polymers. Sparked largely by potential applications in microelectronics, such as thin film transistors and Schottky diodes, it was soon realised that some of these polymers also displayed photoluminescent properties. Only one year after the seminal discovery, the first encouraging results on light emitting diodes based on semiconducting polymers were reported by Burrouges et al. and confirmed by Braun et al. These discoveries triggered intensive academic as well as industrial efforts to understand, develop and eventually commercialise polymer electronic devices.
Presently, conjugated polymers are used as active material in a wide variety of prototype applications, including sensors, photovoltaic devices, and memory cells\textsuperscript{11} to mention just a few. The most promising applications, though, are still the polymer light emitting diodes (LEDs) and thin film transistors, given the current high interest in developing ultra thin computer monitors and television sets, i.e. flat-panel displays.

1.2 My Work

Despite tremendous achievements, the field of conjugated polymers is still in its infancy, mimicking the more mature inorganic, i.e. silicon-based, technologies. We may though look forward to the realisation of electronic and electrochemical devices with exotic designs and device applications, as our knowledge about the fundamentals of these promising materials grow ever stronger.

My own contribution to this development, originating from an idea first put forward by my tutor, Professor Magnus Berggren, is a design for a switchable polymer-based diode. Its architecture is based on a modified version of a recently developed highly-rectifying diode\textsuperscript{12}, where an intermediate molecular layer has been incorporated in the bottom contact. Due to its unique ability to switch its internal resistance during operation or upon external stimuli, this thin layer can be used to control the amount of (forward) current induced into the active polymer layer of the device. Such a component should be of commercial interest in display-technologies since it would, at least hypothetically, be able to replace the transistors presently used to address the individual matrix elements.

However, although fairly simple in theory, it proved to be quite the challenge to fabricate the device structure. Machinery errors and contact problems aside, several process routes needed to be evaluated and only a small fraction of the batches were successful. In fact, it was not until the very last day that I detected the first indications that the concept might actually work. Hence, several modifications might still be necessary to undertake in order to get the device to work properly.

1.3 Approach

In this diploma work, I have tried to bring together in one place the results of a relatively large number of studies on conjugated polymers, as well as metal-polymer interfaces, in an attempt to produce a simple and coherent picture of some of the unique features important in understanding and controlling the performance of solid state polymer-based electronics. Thus, in addition to its primary use as an introductory text on solid state organic electronics (and a survey of my own small contribution to the field), the references provided should be sufficient to enable the interested reader to delve deeper into the area.

1.4 Structure and Organisation

In addition to the present ‘General Introduction’ chapter, the contents are organised and presented in chapters, and subdivided in such a way that, to the extent reasonably possible, each chapter comprises a free-standing unit, which may be read (by readers of appropriate background\textsuperscript{1}) as independent units, if or when necessary.

\textsuperscript{1} With appropriate background means that the text is geared for students and graduates who has completed a calculus-based elementary course in classical physics and intermediate courses in non-classical physics and semiconductor technology.
The introductory chapters (2 and 3) represent an attempt to illustrate the state-of-the-art of basic physics and material science of conjugated polymers and their interfaces, which may be relevant in the context of the emerging area of polymer-based electronics, in general, and polymer-based rectifying diodes in particular. This material provides the sufficient background necessary to understand the device properties of the switchable polymer diode presented in Chapter 4.

Generally, but especially in the introductory and background material, the discussions are made as short, concise and to-the-point as possible, pointing out the features relevant to the specific topics at hand.
2.1 Introduction

The semiconductor materials used in this diploma work belong to a special group of polymers commonly referred to as conjugated polymers. They distinguish themselves from the standard, insulating organic polymers through their $sp^2$-hybridised carbon backbone (see Section 2.2). If the $p_z$-orbitals containing the conduction electrons overlap along the backbone, these materials will display properties resembling those of inorganic semiconductors. However, due to strong electron(hole)-lattice coupling, the charge storage mechanism within these essentially one-dimensional chains differs significantly from those of the rigid band semiconductors (see Section 2.3). Moreover, the lack of three-dimensional order in the solid state makes the matter of charge carrier transportation within the bulk material fairly complex, as can be understood from Section 2.4.

2.2 The Case of Polyacetylene

Polyacetylene, first synthesised in 1956 by Natta et al., is the simplest conjugated polymer known, consisting of a planar or near planar chain of CH repeat units with $sp^2$ hybridised carbons along its backbone. Due to the trigonal planar nature of the $sp^2$ orbital lobes (120 degrees apart and in a plane) three different isomers, i.e. geometrical configurations, of polyacetylene exists: cis-transoid, trans-cisoid and trans-transoid. Here, however, only the trans-transoid version of the polymer, commonly referred to as trans-polyacetylene, will be considered since both the cis-transoid and trans-cisoid isomer is energetically unfavourable compared to the trans-transoid form. This isomer, characterised by its zigzag backbone structure, is depicted below in Figure 2.1.
A simple MO (molecular orbital) representation of (a) σ-bonds and (b) π-bonds in trans-polyacetylene.

As for most conjugated polymers, the chain consists of hydrocarbons, in which the orbitals of the carbon atoms are arranged in such a way that the 2s, 2p_x, and 2p_y orbitals combine to three sp^2 hybrid orbitals which host three of the four valance electrons from each carbon atom. The three sp^2-hybridised orbitals constitute three lobes, symmetrically directed in the xy-plane, that form σ-bonds with neighbouring carbons and hydrogens. Within one-electron theory, this would, in the limit of an infinite polyene, correspond to σ-type and π-type energy bands with the π-band closest to the gap between the highest occupied molecular orbital (HOMO) and the lowest molecular orbital (LUMO). In addition to σ-bonds there are π-bonds formed above and below the xy-plane by the carbon 2p_z-orbitals. Assuming equal C-C bond lengths and a quasi one-dimensional structure this means that the unit of repetition contains one carbon atom that contributes one electron in a 2p_z-orbital to the π-electron system. Since there is room for two electrons in each 2p_z-orbital, due to spin degeneracy, this implies that the π-band is half filled. Trans-polyacetylene should thus be in a metallic state. However, in reality intrinsic trans-polyacetylene displays semiconductor properties.

The first ones to theoretically account for this behaviour were Su, Schrieffer and Heeger (SSH). In a seminal paper from 1979, rejecting previous models that only focused on the π-electrons of the system, they introduced a Hückel type of Hamiltonian (H) that also took into account the σ-electrons, approximated as harmonic potential energy terms due to their localised nature within the hybridised sp^2-orbitals. Thus, in the SSH theory, the Hamiltonian of the system is made up of two components, according to:

\[
H = \sum_i (t_0 + \alpha(u_i - u_{i+1})) (c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i) + \frac{1}{2} \sum_i K(u_{i+1} - u_i)^2 , \tag{2-1}
\]

where \(c_i^\dagger\) denotes the creation operator for an electron in the π-orbital of the \(i\)th carbon atom and the \(u\)’s describes the displacement of carbon sites from their uniform position \(u_i\), all else being constants. Here, the first sum describes the hoppings (see Section 2.4) of π-electrons between adjacent p_z-orbitals of the carbon atoms and the second sum the combined effects of the σ-electrons described by a harmonic potential energy term with a spring constant \(K\). Note that the sums run over all carbon atoms in the chain and the interactions are limited to nearest neighbours.

Since the first summation term in Eq. (2-1) is linearised, the strength of the hopping is proportional to the difference in displacement of the carbon atoms from their equilibrium positions \(u_i\). Direct information about the bond lengths can therefor be obtained from the analytical solution. Using the SSH Hamiltonian to calculate the ground state of trans-polyacetylene thus enabled Su, Schrieffer and Heeger to analytically predict the carbon-carbon bond lengths of the polymer backbone. The results suggested, in accordance with the

\[\text{The values of the constants used in Ref. [16] are } t_0 = -2.5 \text{ eV, } \alpha = 4.1 \text{ eV}/\text{Å and } K = 21 \text{ eV}/\text{Å}^2.\]
findings of Peierls,\textsuperscript{17} that the polymer chain was dimerised with respect to the distribution of π-bonds within the system.

The dimerisation of the backbone is best understood by a simple supposition. Start with the equally spaced carbon chain and suppose that every second atom is displaced a little. This immediately reduces the translational symmetry and doubles the period of the lattice, i.e. the size of the unit cell, from one CH group to two, thus halving the 1:st Brillouin zone (Figure 2.2). Since the new Brillouin zone boundary will coincide with the Fermi wave vector,\textsuperscript{18} the π-band will split into two: one filled (π) and one empty (π*). These two bands, though, will repel each other and thus a band gap, known as the Pierels gap, opens up at the Brillouin zone boundary, where the top of the π-band and the bottom of the π*-band corresponds to the HOMO and LUMO levels, respectively. Since the occupied π-band is lowered in energy, a spontaneous distortion occurs in which the atoms close up in pairs along the chain, i.e. a dimerisation. The lowering of the electronic energy is accompanied by an increase of the elastic energy of the chain. The backbone will thus settle at an equilibrium bond-length-alternation along the chain for which the total energy is minimised.

From this supposition it is obvious that \textit{trans}-polyacetylene, due to dimerisation, is a semiconductor.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.2.png}
\caption{The energy band structures of \textit{trans}-polyacetylene for equal bond lengths and alternating bond lengths, respectively.}
\end{figure}

2.3 Charge Storage States in Conjugated Polymers

The intrinsic low dimensional geometrical nature of linear polymer chains, as well as the general properties of conjugated organic polymers that the geometrical structure is dependent upon the ionic state of the molecule (due to strong electron(hole)-lattice interactions), leads to the existence of unusual charge carrying species. These species manifest themselves through either charge transfer doping or optical absorption in the neutral system, as self-localised electronic states with energy levels within the otherwise forbidden bandgap.\textsuperscript{19-23} However, depending upon the symmetry of the polymer ground state energies, i.e. whether the system has a degenerate or non-degenerate ground state, the charge storage mechanisms within the systems differ somewhat. In the following discussion, \textit{trans}-polyacetylene and polyparaphenylene will, due to their fairly simple geometric and electronic structures, be deployed to illustrate the charge transfer effects in degenerate and non-degenerate ground state polymers, respectively.

2.3.1 Degenerate Ground State Polymers

The charge transfer mechanism in \textit{trans}-polyacetylene, i.e. the \textit{trans-transoid} version of the polymer, were first investigated by Su, Schrieffer and Heeger within the perimeters of the
previously discussed SSH model.¹⁶ They found that the charge transfer associated with doping induces a localised geometrical defect that changes the dimerisation from one degenerate ground state (phase A) to the other (phase B), as depicted in Figure 2.3. Since an abrupt discontinuity would have an unfavourably high kinetic energy due to the uncertainty principle, the phase change occurs over a transition region of several carbon atom sites in which bond alternation is suspended,²⁷ thus isolating an unpaired electron. These mediating quasi-particles are referred to as solitons, named after the mathematics which describes their behaviour.¹⁰,²⁰ Since the SSH Hamiltonian possesses charge conjugation symmetry, i.e. changes sign under the transformation $C_n \rightarrow (-1)^n C_n$ such that the energy spectrum of the system is symmetric about zero, the wave function of the soliton is made up of half a LUMO band orbital and half a HOMO band orbital, and lies symmetrically in the middle of the bandgap.

![Neutral Chain](image1.png) ![A Transition Region (Soliton)](image2.png)

**Figure 2.3** The formation of a soliton pair within the transition region in *trans*-polyacetylene.

Since the polymer remains neutral, the soliton behave like chargeless ($S^0$) unpaired spin-carriers ($\frac{1}{2}$). However, other charge storage states are possible. Due to the midgap location of the soliton charge storage state, the energy required to add/remove an electron(hole) to/from the system will decrease, thus governing the formation of either a negatively charged ($S^-$) or a positively charged ($S^+$) soliton. Note that both of the solitons are spinless charge carriers, see Figure 2.4 below.

![Schematic Illustration](image3.png)

**Figure 2.4** A schematic illustration of the three possible soliton states: $S^0$ (neutral), $S^-$ (negative) and $S^+$ (positive).

Although depicted as single species (for convenience), solitons are always created in pairs. This is due to topological constraints, i.e. if the alternation order is changed somewhere along the chain, it must also be changed back since the *trans*-polyacetylene chain is always terminated with a double bond.²⁸ Note, however, that the two conformational phases are energetically equivalent. A pair of solitons can therefore be separated with individual solitons moving freely along the polymer chain. Thus the idea was put forward that charged solitons, rather than electrons or holes, would transport charge in degenerate conjugated polymers.¹⁶

For further details on solitons and their physics, the reader may like to consult the excellent article by W. P. Su.²⁹

¹ Exponentially and theoretically determined to be 10-14 carbon atoms.²⁹,²⁴-²⁶
2.3.2 Non-degenerate Ground State Polymers

Even though many polymers have been found to have a degenerate ground state, for the vast majority of conjugated polymers the bond alternation suspended transition region, i.e. the soliton anti-soliton pair, will have a higher energy than the ground state. Such systems are thus said to have a non-degenerate ground state. Since the higher energy state of the bond alternation reversal is unstable, the resultant change in bond lengths must be such that the phase of the polymer chain remains identical on either side of the defect. Such a species is termed a polaron (P) if it is singly charged or a bipolaron (BP) if it is doubly charged. The theoretical description of both the polaron and the bipolaron can be made from an extension of SSH theory, describing them in terms of confined soliton pairs, but is beyond the scope of this chapter. However, a qualitative understanding of polaronic charge carriers can be achieved by considering those polymers containing aromatic bensene rings, using polypharaphenylene (PPP) as a model system (see Figure 2.5). For simplicity, the p-type doping, i.e. removal of electrons, will be considered.

If an electron is removed from the neutral chain by means of oxidation, i.e. p-type doping, a free radical (i.e. an unpaired electron with spin ½) and a spin-less positive charge (cation) is created, coupled to each other via a localised bond rearrangement which in this case takes the form of a sequence of quinoid rings. Since the quinoid lattice distortion is of higher energy than the remaining portion of the chain, which still retains a bensoid bonding configuration, the number of quinoid rings that can link these two bound species together are limited. This combination of a charged site coupled to a free radical via a local lattice distortion, i.e. a polaron, creates a new localised electronic state within the bandgap, P+, with the lower energy state being occupied by a single unpaired electron of spin ½.†

Upon further oxidation, the free radical of the polaron is removed and a dication is created comprised of two positive charges coupled through the lattice distortion. This new spinless defect is called a positive bipolaron (BP++).‡ At higher doping levels, it also becomes energetically possible for two polarons on the same chain to combine to produce a bipolaron. Thus, additional oxidation is accompanied by the elimination of polarons and the emergence of new localised bipolaron states, which, at high enough doping levels, can overlap to form continuous in-gap bipolaron bands. For conjugated polymers that can be heavily doped, it is theoretically conceivable that the upper and lower bipolaron bands will eventually merge with the LUMO and HOMO bands, respectively, to produce partially filled bands and metallic-like behaviour. It should be noted that a similar mechanism has been proposed for solitons, thus accounting for the high conductivity of highly doped trans-polyacetylene. 

---

*Figure 2.5 The structural modification of the polypharaphenylene (PPP) chain geometry and corresponding changes in the electronic structure for a (a) positive polaron and a (b) positive bipolaron.

† For a negative polaron, created upon reduction, i.e. provision of electrons, of the neutral chain, the state just above the HOMO band is filled and the state bellow the LUMO band is half-filled. It therefor also have spin ½.
‡ In the case of reduction, a negative doubly charged spinless bipolaron (BP−) is created with doubly occupied in-gap energy levels.
2.4 The Electronic Properties of Conjugated Polymer Bulks

As previously pointed out, the charge storage states, in conjugated polymers are, due to the strong electron-phonon coupling, localised within the bandgap. Charge carrier transport can therefore not be achieved by spatially free moving (Bloch) electrons. The first one to point this out was P. W. Anderson. In a classical paper from 1958, he showed that the transport of electrons between localised states in a highly disordered solid is done with the help of thermally excited lattice vibrations, i.e., phonons, in a phonon-assisted quantum tunnelling event called hopping (see Section 2.4.3). However, due to the finite range of phonon energies, set by the temperature, the mean free path of an electron, commonly referred to as the localisation length, will be limited by the number of energetically accessible states. In such a case the one-electron wave function takes on an exponential form \( \psi(r) = e^{-|r|/\lambda} \), where \(|r|\) is the distance from the centre of the localised wave and \( \lambda \) the size of the localised state.

Using a tight binding model with nearest neighbour interaction

\[
H = \sum_{l} \varepsilon_{l} |i\rangle \langle i| + \sum_{i,j<i} |i\rangle \langle i+1| + |i+1\rangle \langle i|,
\]

(2-2)

where disorder is represented by random onsite energies \( \varepsilon_{l} \), Anderson was able to show that the wave function in a one-dimensional lattice localises for any non-zero disorder, i.e., \( w > 0 \). One-parameter scaling theory predicts an equivalent behaviour for two-dimensional systems. In three-dimensional lattices, however, there is a mobility edge (energy) that separates localised and extended states in the energy spectrum and a transition from localised to extended states can be observed as the amount of disorder is reduced. This corresponds to a transition from an insulating to a metallic state.

Numerically, most studies on the Anderson localisation has been conducted on cubic lattice systems with isotropic hopping and randomly on-site energies. These models are, however, unlikely to describe the behaviour of conjugated polymer materials, since the weak interchain hopping perpendicular to the chain direction \( (r^\perp) \) compared to the intrachain hopping strength \( (r^\parallel \sim t_{0} - (u_{k+1,l,m} - u_{k,l,m}) ) \) renders the system highly anisotropic with a dimensionality closer to one than three. Such quasi-1D systems are well described by a simplified (one-electron) tight-binding Hamiltonian with nearest neighbour hopping

\[
H = \sum_{k,l,m} \varepsilon_{k,l,m} |k,l,m\rangle \langle k,l,m| + H.c.
\]

(2-3)

Here, the sum is to be taken over a 3D cubic lattice, where \( |k,l,m\rangle \) denotes the orbitals at the site along the chains \( (k) \) and in a plane perpendicular to the chain axis \( (l,m) \).

This system is depicted in Figure 2.6 as a bar with a finite quadratic cross section \( M \times M \), where \( M \) is the number of (1D) chains in each direction perpendicular to the chain axis. Note that since all types of conjugated polymers can be mapped onto a one-dimensional chain by a renormalisation argument, the results presented in the following sections should provide a qualitatively correct picture of localisation in conjugated polymers in general.
The 3D cubic lattice of weakly coupled polymer chains have been modelled as a ‘bar’ with a quadratic cross section $M \times M$, where $M$ is the number of chains in each direction perpendicular to the chain axis. Note that the hopping strength along the chain axis ($t^1$) are much stronger than the hopping perpendicular to the chain direction ($t^\perp$), thus rendering the system anisotropic.

**2.4.1 Localisation Lengths and the Metal-Insulator Transition**

The localisation length of the one-electron wave function in disordered systems of coupled chains have successfully been studied using the transfer matrix method. In brief, the theory predicts that the evolution of an electronic state throughout the system can be described as

$$Q_n = \prod_{k=1}^{n} T_k ,$$

where $T_k$ denotes a transfer matrix, acquired through iteration of the (2D) time-independent Schrödinger equation in the tight-binding approximation, that connects the coefficients of the wave function in a slice $k$ of the bar with its value on the nearest-neighbour slice. From this result the transmittance, reflectance and conductance of the bar can, in principle, be calculated using, e.g., the Landauer formula.

However, due to the numerical instability given by the exponentially increasing/decreasing eigenvalues of the transfer matrix, this product cannot be used directly to determine whether or not the wave function is localised. Instead the Lyapunov characteristic exponents (LCE) $\gamma$, obtained from the eigenvalues $\exp(\gamma)$ of the limiting matrix

$$\Gamma = \lim_{n \to \infty} (Q_n Q_\dagger)^{1/2n} ,$$

may be calculated, since the localisation length $\lambda_M$ in a bar of cross section $M \times M$ can be calculated as the inverse of the smallest positive LCE greater than one. However, in order to extrapolate and answer the question whether or not the states at the Fermi level localises in the infinite system, one must study the finite size scaling behaviour of the renormalised localisation length $\Lambda_M = \lambda_M / M$ as a function of the width $M$ of the bar. If $\Lambda_M$ decreases with increasing $M$, then the wave function is localised, while, correspondingly, if $\Lambda_M$ increases with increasing $M$, the wave function is extended. Clearly a transition occurs at $\delta\Lambda_M/\delta M=0$ between localised and delocalised states that transits the material from an insulating to a metallic phase.

† The limiting matrix follows from a theorem of Oseledec, provided that the determinant of every $T_k$ is finite and nonzero.

‡ Note that since the eigenvalues of $\Gamma$ may differ by several orders of magnitude, numerical difficulties often arise in determining the smallest LCE. This problem, though, can be overcome by using an orthogonalisation process suggested by Bennetin and Galgani.

The Fermi level were calculated from the band structure of a single chain, $E_k = \varepsilon + 2 t^1 \cos(k_x) + \cos(k_y) + \cos(k_z)$, adding the dispersion $2 t^\perp [\cos(k_x) + \cos(k_y) + \cos(k_z)]$ to calculate the 3D band gap.
2.4.2 Effects of Doping and Interchain Interactions on the Metal-Insulator Transition

The metal-insulator phase transition (MIT) boundary for trans-polyacetylene has recently been calculated by Paulsson and Stafström as a function of disorder concentration ($w$) and as a function of the soliton concentration ($y$) and interchain interaction strength ($r^\perp$). Using a tight-binding Hamiltonian model, i.e. Eq. (2-3), they found that: (i) an increased soliton concentration lowers the value of $r^\perp$ needed to delocalise the wave function, and (ii) that the parameter space $R \in (y, r^\perp)$ that involves the metallic region is reduced by disorder (see Figure 2.7).

![Figure 2.7](image)

Figure 2.7 Schematic metal-insulator phase diagram showing the amount of disorder ($w$) needed to localise the wave functions for different interchain coupling strength ($r^\perp$) and soliton concentration ($y$). Note that the boundaries between localised (lower left) and delocalised states (upper right) for different amounts of chain breaks are indicated by the lines.

In order to explain these results the theory of hopping, i.e., the phonon assisted quantum mechanical tunnelling of electrons between adjacent sites within the polymer ‘lattice’, needs to be capitalised. According to this theory, the probability of a jump, in the presence of an applied external bias, i.e., electric field ($F_e$), is given by the equation:

$$v_{hop} = v_{ph} e^{-[2\alpha + (W + qF_e \beta / k_B T)]},$$

where $v_{ph}$ is the hopping attempt frequency, $\alpha$ is the inverse localisation length of the localised state wave function, $R$ the distance between the two sites, $W$ is the energy difference between the states, and $k_B$ and $T$ are the Boltzmann constant and temperature, respectively. Note that the first term in the exponential accounts for the tunnelling probability between the states, while the second term (in the ‘special case’ of $F_e=0$) is the Boltzmann factor indicating the probability that an electron has enough energy to reach the other state.

From Eq. (2-6) it should be evident that (i) can be accounted for by an increase in probability of jumps as the hopping distance ($R$), due to the increase in density of states (DOS) at the Fermi level, i.e., the soliton concentration ($y$), decreases. With smaller hopping distances, and hence greater hopping transition probabilities, a less strong (mean) interchain hopping strength ($r^\perp$) is required to maintain the critical conditions of the MIT, hence the negative slopes of the curvatures in Figure 2.7. When disorder is introduced (ii), the ensuing interference from the elastically scattered wave functions results in increased potential

---

† In which disorder is introduced by setting the hopping strength along the chain ($t^\parallel$) to a small value ($t^\perp$) between randomly chosen adjacent sites with a given concentration ($w$), and the geometrical disturbances of the solitons by setting the displacements of the carbon atoms to

$$u_k = (-1)^k u_0, \prod_n \tanh \left[ \frac{k - x_n}{7.0} \right],$$

where $x_n$ is the position of the soliton.
barriers for electron tunnelling. The probability of jumps therefore decreases as the disorder concentration \( w \) increases, and either a greater interchain hopping strength or an increased soliton concentration is required to maintain the critical conditions of the MIT. This is accounted for in the (2D) diagram as the displacement of the MIT boarder for different amounts of disorder.

2.4.3 Effects of Localisation and Structural Disorder on Conductivity

Despite the seemingly good comprehension of transport related topics within conjugated polymers, no consistent theory of conduction yet exists that accurately predicts the current densities over the hole conductivity range, i.e., from insulator to metal. Instead, a dual conduction model that emanates from the different possible arrangements of disorder in the polymers has been adopted. According to this, disorder is either homogeneously\(^4\) or heterogeneously\(^4\) distributed throughout the sample, depending on the doping concentration.\(^\dagger\)

When lightly or moderately doped, the homogeneous model applies and the interesting properties of conduction is controlled by Anderson localisation in the bulk, while at higher doping concentrations the heterogeneous model more accurately describes the current transport processes. In the following the details of these two models will be outlined.

In the case of homogeneously distributed disorder, charge transport is explained by hopping between localised states within the band gap, in accordance with Eq. (2-6). Depending on the degree of localisation though, the contribution of the exponent \( e^{-2\alpha R} \), which arises from the wave function overlap, differs somewhat. In the case of strong localisation, i.e., \( \alpha R_0 \gg 1 \), where \( R_0 \) is the nearest neighbour distance, only nearest neighbour hopping is possible.\(^4\) However, if \( \alpha R_0 \lesssim 1 \) (or at very low temperatures \( T \)), the localisation of states are weak and the electrons are able to jump further away than the nearest site. In such a case the conductivity has been shown\(^50,51\) to approximately follow the Variable Range Hopping (VRH)\(^52\) type of behaviour with dc conductivity

\[
\sigma(T) = \sigma_0(T) e^{-\frac{U_0}{T/T_0^{1/\alpha}}} 
\]

(2-7)

where the characteristic temperature \( T_0 \), for a \( d \)-dimensional system, is related to the density of localised states \( N(E_F) \) and the localisation length \( \lambda \) as \( T_0\approx (\lambda^d \cdot N(E_F))^{-1} \). Note, though, that the VRH theory does not specifically deal with the unique charge carriers that exists in conjugated polymers. This was first addressed by Kivelson in his intersoliton hopping theory,\(^53\) and later on extended and modified by Kuivalainen et al.\(^54\) to account for interpolaronic conduction in non-degenerate ground state polymers. There also exist a bipolaron hopping model derived by Chance et al.\(^55\)

Although successful in describing the conductivity of lightly and moderately doped samples, hopping theory fails to account for the higher conductivity found in highly doped conjugated polymers,\(^56-60\) mainly due to the changes in disorder distribution. Instead a model with small conducting islands with metallic conductivity separated by insulating barriers (i.e., the heterogeneous model) is used. Charge transport through the material will then be limited by the fact that the charge carriers have to tunnel through these barriers. The most successful theories so far describing this type of conductivity have been presented by Sheng.\(^61,64\) For small conducting islands (typically with dimensions smaller than 20 nm) the temperature dependence of the conductivity can be written as:\(^63\)

\[
\sigma(T) = \sigma_0 e^{-\frac{U_0}{T/T_0^{1/\alpha}}}, 
\]

(2-8)

\(^\dagger\) Doping is here a misnomer as it tends to imply the use of minute quantities, e.g. parts per million or less, of impurities introduced into a lattice. This could not be further from the truth. In the case of conjugated polymers, typically 1% to 50% by weight of chemical oxidising (electron withdrawing) or reducing (electron donating) agents are used to physically alter the number of \( \pi \)-electrons on the polymer backbone.\(^58\)
where $\sigma_0$ and $T_0$ are material constants. If the conducting islands are larger (microns), the expression for conductivity changes to: \(^{64}\)

$$\sigma(T) = \sigma_0 \ e^{-T_1/(T_2+T)},$$

(2-9)

where $T_1$ and $T_2$ are constants dependent on the width and height of the tunnelling barrier. Note that it is often difficult to distinguish between the different cases outlined above, since experimental values can be fitted reasonably well to both when, as is often the case, the temperature range is limited and does not include temperatures close enough to absolute zero.
3.1 Introduction

In the device applications in mind for this diploma work, the material properties of the previously discussed conjugated polymers are electrically addressed through metallic contacts over the metal-polymer interfaces. By proper choice of contact materials, the interfacial properties of these junctions have been manipulated in such a way as to achieve high rectification of current flow through the component. The models presently used to describe such devices, commonly referred to as diodes, are thus briefly discussed in Section 3.2 and modified for non-ideal field contributions, i.e., real world applications, in Section 3.3. These two sections provide the proper foundation for a subsequent analytical discussion on the limitations on charge flow across these interfaces (see Section 3.4), from which a fairly coherent description of the current-voltage ($I/V$) characteristics can be deduced.

3.2 Diode Models

For polymer based diode structures, where the conjugated polymer is sandwiched between two metal electrodes, simplified models based on approximations regarding the conductive nature of the organic has been proposed that displays fairly good contingency with experimental results. Accordingly, the arrangement can be described either as a metal/semiconductor/metal (MSM) or a metal/insulator/metal (MIM) device, depending on whether or not the free charge carrier concentration (intrinsic or extrinsic) is above or below $10^{17}$ cm$^{-3}$. The physics of these two systems provides a starting point on explaining device performance and will thus be outlined below.
3.2.1 Devices from Conjugated Polymers with a High Defect Concentration

In modelling devices of conjugated polymers with a high charge carrier concentration \( (n > 10^{17} \text{ cm}^{-3}) \), sandwiched between two metal electrodes, the organic is treated as a p-type semiconductor. The general electrical behaviour of the device can thus be understood in terms of traditional metal-semiconductor theory, as outlined below.

When a metal is brought into electrical contact with a p-type polymer semiconductor having a work function larger than that of the metal, i.e. \( \phi_\text{p} > \phi_\text{m} \), holes flow from the HOMO-level of the polymer into the metal, leaving behind a depleted region of uncompensated negative acceptor ions and causing an accumulation of holes on the metal side of the boundary. Consequently, when equilibrium is reached, i.e. \( dE_\text{F}/dx=0 \), the energies of holes at rest outside the two solids are no longer the same, and there exists a built-in potential \( V_{\text{Bi}} \) across the junction equal to the lowering of the polymer Fermi level

\[
qV_{\text{Bi}} = \phi_\text{p} - \phi_\text{m},
\]

where \( V_{\text{Bi}} \) is measured in volts. Since the vacuum level must remain continuos throughout the entire metal-polymer system,\(^{71}\) the energy bands across the depleted space charge region, over which the potential drop occur, are bent downwards (see Figure 3.1a). \( qV_{\text{Bi}} \) is thus the potential barrier which a hole moving from the polymer into the metal has to surmount.

At equilibrium, the rate at which the holes cross over the barrier from the polymer into the metal is balanced by the rate at which the holes cross the barrier in the opposite direction and no net current flows. If an external bias \( V_\alpha \) is applied to the device essentially all potential drop would appear across the depleted region due to its low concentration of mobile carriers and hence high resistivity. This would alter the equilibrium band diagram by changing the total curvature of the bands and thus, depending on the polarity of the applied bias, either increase \( (V_\alpha < 0) \) or reduce \( (V_\alpha > 0) \) the potential barrier for the hole flow \( (V_{\text{Bi}} - V_\alpha) \) from the polymer into the metal. The barrier looking from the metal towards the semiconductor, though, is independent on the applied bias and remains at its equilibrium value given by the Mott-Schottky equation:\(^{72,73}\)

\[
\phi_{\text{BP}} = (E_g / q) - (\phi_\text{m} - \chi_\text{p}),
\]

where \( E_g \) is the semiconductor bandgap and \( \chi_\text{p} \) is the polymer electron affinity. Thus, while the charge carrier flow from the polymer towards the metal may be either increased \( (V_\alpha > 0) \) or reduced \( (V_\alpha < 0) \), the flow from the metal remains practically unchanged. Due to the asymmetry in charge flow between a forward biased \( (V_\alpha > 0) \) and a reverse bias \( (V_\alpha < 0) \) junction, the contact under discussion is a rectifying metal-polymer contact. It should be noted that if the p-type polymer in above had been substituted with an n-type polymer, no depleted region would have developed and instead of a rectifying behaviour, a linear \( I/V \) characteristic,\(^{74}\) independent of bias polarity, would have been obtained. Such a contact is said to be ohmic.

**Figure 3.1** Schematic band structure of the single-layer (high defect) polymer device as a function of applied voltage: (a) equilibrium \( (V_\alpha = 0) \); (b) forward biased \( (V_\alpha > V_{\text{Bi}}) \); and (c) reversed bias \( (V_\alpha < V_{\text{Bi}}) \).
3.2.2 Devices from Conjugated Polymers with a Low Defect Concentration

For a conjugated polymer with a low defect concentration \((n < 10^{17} \text{ cm}^{-3})\), sandwiched between two metal electrodes, the lack of mobile carriers within the active layer renders it almost insulating with a very high resistance. A situation resembling that of a charged capacitor thus occur, where the contact potential drop over the polymer layer is solely determined by the difference in the work function of the two metals prior to contact, i.e. \(V_{Bi} = \phi_{m1} - \phi_{m2}\), as depicted in Figure 3.2a. In this particular case both metals serve as hole-injecting contacts and the device is thus hole-conducting only.

When an external bias voltage \((V_a)\) is applied to the system, the potential drop across the organic layer is modified according to \((V_{Bi} - V_a)\). For an applied bias of less than \(V_{Bi}\), the electric field inside the polymer opposes charge injection over the left-hand potential barrier, \(\phi_{\text{hp, anode}}\). In the case when the applied voltage equals the difference in the work function of the two metals, the so-called flat band condition is obtained (see Figure 3.2b). When the applied voltage exceeds this value, the width of the potential barrier for charge injection decreases and at some critical field, charge injection into the polymer becomes possible (Figure 3.2c). Under reverse bias the barrier for charge injection, \(\phi_{\text{hp, cathode}}\), is high and little current flows through the device (Figure 3.2d). Due to the uneven charge flow across the junctions under different applied voltage polarity, the device is rectifying.

![Figure 3.2](image_url)

**Figure 3.2** Schematic band structure of the single-layer (low defect) polymer device as a function of applied voltage: (a) zero bias; (b) flat band condition \((V_a = V_{Bi})\); (c) conducting state \((V_a > V_{Bi})\); and (d) reverse conductive state \((V_a < V_{Bi})\).

3.3 The Field Dependence on the Barrier Height

Due to non-ideal electric field contributions normally present within the junction, practical metal-polymer contacts generally do not obey the above guidelines, particularly not Eq. (3-2). The origin of these anomalies has been thoroughly investigated and several independent as well as cross-related effects have been identified. Among the most important ones are that due to the presence of thin interfacial layers at the junction, unintentionally introduced either through chemical cleaning of the anode metal electrode or through chemical reactions between vapour-deposited cathode metal atoms and the organic molecules at the surface of the polymer film. The origin of these anomalies has been thoroughly investigated and several independent as well as cross-related effects have been identified. Among the most important ones are that due to the presence of thin interfacial layers at the junction, unintentionally introduced either through chemical cleaning of the anode metal electrode or through chemical reactions between vapour-deposited cathode metal atoms and the organic molecules at the surface of the polymer film. The origin of these anomalies has been thoroughly investigated and several independent as well as cross-related effects have been identified. Among the most important ones are that due to the presence of thin interfacial layers at the junction, unintentionally introduced either through chemical cleaning of the anode metal electrode or through chemical reactions between vapour-deposited cathode metal atoms and the organic molecules at the surface of the polymer film. The generalised analysis of metal-semiconductor contacts in the presence of surface states and interfacial layer revealed that the presence of electric field in the polymer at zero applied bias alters the potential drop in the interfacial layer and thus decreases the barrier height in accordance with the relation

\[
\phi_{\text{hp}} = E_G + \chi_p - \phi_m - V_i = \phi_{\text{hp}}^0 - \alpha E_c \text{max} = \gamma (E_G - (\phi_m - \chi_p)) + (1 - \gamma) \phi_c - \alpha E_c \text{max},
\]

where

\[
\alpha = \frac{\delta E_i}{E_i + q\delta D_x} \quad \text{and} \quad \gamma = \frac{E_j}{E_i + q\delta D_x}.
\]
Here $\phi_{BP}$ is the barrier height at flat band condition, $\phi_o$ is the natural level of surface states, $D_s$ is the density of surface states, and $\delta$ is the width of the interfacial layer. When the electric field penetration into the metal (confined within the Thomas-Fermi screening distance $r_o$ of the surface) is taken into account, the interfacial layer width $\delta$ in Eq. (3-3) is expanded into $\delta + (r_o \epsilon / \epsilon_0)$. This is schematically illustrated in Figure 3.3.

**Figure 3.3** Schematic band structure of the single-layer (high defect) polymer device in the presence of a thin interface layer and pined Fermi level.

Independent on whether an interfacial layer is present or not, a charge carrier trying to traverse the barrier will experience an attractive Coulomb image force $q^2 / 4 \pi \epsilon \epsilon_0 (2x)^2 = q^2 / 16 \pi \epsilon \epsilon_0 x^2$ that pulls the hole towards the surface of the metal, thus lowering its potential energy by an amount

$$qV_f = \frac{1}{q} \int qF \, dx = -\frac{q^2}{16 \pi \epsilon \epsilon_0 x}$$

relative that of a hole at infinity. This potential energy has to be added to the potential energy $-qF_{ex}$ to obtain the total energy of the hole. From Poission’s equation it can be shown that the maximum field strength $[2qN_d(V_{B1}-V_a)/\epsilon \epsilon_0]^{1/2}$ occurs at a distance $x_m$ into the organic at the junction. Since the potential energies of the image force and the electric field exactly cancel each other, that is $F_{ex\ max} = qV_f / qx_m$, the magnitude $\Delta \phi_{BP}$ of the potential barrier lowering (as depicted in Figure 3.4) is given by

$$\Delta \phi_{BP}(x_m) = \frac{q^3 N_d}{8 \pi^2 (\epsilon \epsilon_0)^2 \epsilon_s} \left( V_{B1} - V_a \right)$$

where $N_d$ is the donor concentration in the semiconductor, and $V_a$ is the applied external bias.
In the close vicinity of the electrode, i.e. within the region $0 < x < x_m$, the strongly negative image force potential enables the existence of bound bipolaron states that for sufficiently high density of chains at the metal electrode (i.e. $D = 10^{18} \text{ m}^{-2}$) organises into a lattice.\textsuperscript{85,86} Since almost all trapped charges in this lattice are centred in the first polymer layer from the interface, at $x = x_1$, it is a valid first approximation to treat the lattice as composed of only one layer. The presence of such a layer, in turn, modifies the potential energy for charge emission $\chi_p(x) - E_{Fm}$ by a summation factor of $qS(x)$, where

$$S(x) = \frac{1}{4\pi \varepsilon \varepsilon_0} \sum_i \left[ \frac{q_i}{\sqrt{r_i^2 + (x - x_i)^2}} - \frac{q_i}{\sqrt{r_i^2 + (x + x_i)^2}} \right],$$

is a series of Coulombic terms originating from the different trapped charges.\textsuperscript{†} Here $q_i (= q)$ are the different trapped charges centred at the distance $x_i$ from the interface and occupying the site $\mathbf{r}_i$ in the plane parallel to this interface.\textsuperscript{‡}

### 3.4 Current Transport Processes

When analysing the electrical characteristics in metal-polymer contacts, it is commonly distinguished between contact limited currents and space charge limited currents. At low fields, or for high enough potential barriers ($\phi_{Bp, r} > 0.3 \text{ eV}$), the current, i.e. the number of charge carriers injected into the bulk per second, is limited by the height of the potential barrier, and the current regime is thus said to be contact limited. Raising the applied field strength will eventually lead to a situation where the polymer material no longer is able to transport injected charge carriers sufficiently fast across the bulk. A space charge will thus arise within the bulk, and the current regime is said to be space charge limited. In subsequent sections, the $I/V$ characteristics of these two regimes will be further investigated.

\textsuperscript{†} Note that the typical concentration of occupied sites in the first layer is of 5%, which allows one to neglect the interactions between bipolarons but require one to treat the discreteness of the bipolaron lattice explicitly.\textsuperscript{87}

\textsuperscript{‡} Note that the image force potential for each trapped charge is included.
3.4.1 Charge Carrier Injection / Contact Limited Currents

With very few exceptions, all early attempts to model injection limiting contacts in low defect polymer-based diodes have relied on the Fowler-Nordheim field emission model, where the charge injection occurs at high fields by tunnelling through a triangular barrier into unbound continuum states. It predicts, at 0 K, that the current density \((J)\) dependence on field \((F_e)\) is described by the expression:

\[
J(F_e) = \frac{A'' q^2}{\phi_B (ak_B)^2} F_e^2 e^{-\frac{4\sqrt{2m_e\phi_B}}{q\hbar k_B}},
\]

where \(A''\) is a material parameter, \(F_e\) is the electric field, \(q\) is the charge of the electron, \(k_B\) is the Boltzmann constant, \(h\) is the Planck constant, \(\phi_B\) is the potential barrier height, and \(m_e\) is the effective mass of the charge carrier. When the electric-field induced tunnelling currents are analysed in a \(\log(I/IF_e^2)\) versus \((1/F_e)\) plot, theoretical predictions then states that a straight line should be obtained.

This shape of current density dependence on field has been found for many polymer-based structures, as first described by Parker, but the absolute currents are order of magnitudes lower than expected on basis of the Fowler-Nordheim equation. This was first accounted for by considering a backflowing interface recombination current toward the electrode that are the time reversed process of thermionic emission. It is, however, hard to justify the reasons why charge carriers that have tunelled into a region beyond the maximum of the potential should return to the electrode without being impeded by the same energy barrier which the have just passed.

Abkowitz et al. developed an alternative model based on thermally assisted tunnelling that takes proper account of the hopping character of carriers in motion inside the dielectric but ignores both the Coulombic potential and the energetic disorder of the system. They showed that experimental \(j(F)\) curves can be fitted with a reasonable set of parameters provided that non-nearest neighbour transitions, i.e. tunnelling, are invoked. A more sophisticated version of this injection concept has been presented by Gartstein and Conwell employing Monte Carlo simulation techniques. Their model takes full account of both the energetic disorder of any non-crystalline hopping system and the image charge potential and allows evaluation of the probability of a carrier to avoid geminate recombination with its sibling image charge, but without considering the initial injection process. Since this is the energetically most costly event, as pointed out by Bässler, this procedure cannot yield the temperature dependence of the entire injection process.

Based on the thoughts and models presented above, a complete description of the field and temperature dependence of the injection current has to consider the field and temperature dependencies of the primary injection event and of the subsequent random walk of the carriers with the superimposed external and image charge potential, and also take proper care of peculiarities of charge carrier hopping in a random media. Elaborating upon these ideas, Arkhipov et al. presented an analytical theory of charge injection from a metallic electrode into an energetically as well as positionally random hopping system. They found that the initial injection process populates a state within the tail of the density of states (DOS) of the hopping sites, and that it therefore can be assumed that thermal quasi-equilibrium is already established when the carrier starts its random walk. Under this premise, escape from geminate recombination with its image charge can be treated in terms of

---

1. The \(\log(I/IF_e^2)\) versus \((1/F_e)\) are usually referred to as a Fowler-Nordheim plot.

2. … with the exception of some deviations in the low-field regime of the plot, later explained by taking in account the temperature dependent (Fermi) distribution of charge carriers in the metallic electrode.

3. The thermionic emission model states that a charge carrier from the metal can be injected into the semiconductor once it has acquired a thermal energy sufficient to cross the potential barrier maximum.
Onsager’s theory of geminate pair dissociation, and concomitantly, the injection current density, \(j(T)\), can be written
\[
j_{j_0} = \frac{e}{\hbar} \int_0^\infty \frac{dE}{E} \exp(-\gamma E)w_{esc}(x_0) \cdot \frac{\partial}{\partial E} \text{Bol}(E') g(U_0(x_0) - E'). \tag{3-8}
\]
Here, \(w_{esc}\) is the probability for a carrier to avoid surface recombination, \(d_0\) the distance from the electrode to the first hopping site in the bulk, \(v_0\) the attempt-to-jump frequency, \(\gamma\) the inverse localisation radius, and the function \(\text{Bol}(E')\), defined as
\[
\text{Bol}(E') = \begin{cases} 
  e^{-E/\kappa T}, & E > 0, \\
  1, & E < 0,
\end{cases}
\]
describes the energy dependence of the jump rate into a Gaussian density of states (DOS) distribution \(g[U_0(x_0) - E']\). The main conclusion of the model are that at high electric fields the calculated current has the Fowler-Nordheim tunnelling form (although tunnelling was not explicitly included in the theory) and that disorder enhances the injection current.

### 3.4.2 Space Charge Limited Currents

The bulk limited or space charge limited current (SCLC) is achieved when one of the electrodes supply more current than the semiconductor can transport and the exit contact can not inject sufficient opposite charge carriers to compensate for the internal space charge. Often this is the case of conjugated polymers because of their low charge carrier mobility. \(^{109}\) \(^{110}\) \(^{111}\) When the electrode forms a low potential barrier (\(\phi_B < 0.3\) eV) \(^{112}\) to the semiconducting material and guarantee enough charge injection to achieve SCLC currents at high fields the electrode is considered ‘ohmic’. However, in order to analytically describe such currents, the concept of charge transport in conjugated polymers needs to be reviewed.

The process of charge transport has been extensively studied in the past in connection with the application of organic materials in electrophotography. \(^{113}\) Charge transport in these materials takes place via hopping, with each hopping site located in a statistically different environment due to the lack of long-range order. As a result, there is a distribution in both site distance and energies (as previously discussed). Theories (such as the Bässler formalism a.k.a. Gaussian disorder model) that use this postulate as starting point, have been quite successful in describing the charge transport characteristics of molecularly doped polymers and organic glasses, \(^{113}\) although their applicability for the case of conjugated polymers, is still a matter of debate. \(^{114}\) \(^{115}\) The main consequence of disorder is that the mobility displays an electric field dependency and can frequently be described according to:
\[
\mu = \mu_0 \cdot e^{F_0 / \kappa T}, \tag{3-9}
\]
where \(\mu_0\) is the zero field mobility and \(F_0\) a characteristic field.

Using an analytical one-dimensional model, Dunlap et al. \(^{116}\) suggested that this dependence (often called Poole-Frenkle like) arises from energetic disorder and randomly located dipoles in the amorphous medium. \(^{116}\) Because of the long range nature of the dipolar field, the energy on neighbouring sites is somewhat correlated, and it is the nature of this correlation that gives rise to the electric field dependence. Recent simulations of the three-dimensional system confirm this result. \(^{117}\) Nevertheless, experimental observations of the mobility in systems without strong dipoles \(^{118}\) \(^{119}\) indicate that this model cannot serve as an explanation for the whole class of materials.

An alternative model, similar to the one used by Dunlap et al. \(^{116}\) was developed by Blom et al. \(^{130}\) for which the characteristic field dependence of the mobility follows directly from the topology of the inhomogeneous structure. They proposed that due to the strong localisation of charge carriers in disordered materials, relatively modest variations in
structural order, e.g. in density or alignment of molecules, give rise to large variations in electronic coupling between clusters of molecules. This enables one to model the system as being composed of relatively ordered clusters of sites with negligible internal resistance, that act as reservoirs of charge carriers, connected in series through parallel one-dimensional percolating paths that govern the conductivity of the material.\textsuperscript{†} Carriers trying to traverse the bulk will get caught in the ordered regions, bouncing forward and backward with zero net velocity for a period of time before they escape.\textsuperscript{122} When this time is sufficiently long, the ordered region contains a large amount of equilibrated carriers and acts as a reservoir of charge. In escaping these reservoirs, the process of returning is effectively suppressed by the potential energy difference $qF_c l$, where $l$ is the distance that the carrier has escaped form a reservoir, which leads to a strong increase in charge carrier mobility at relatively low fields. These findings are in agreement with experimental results.\textsuperscript{120,121} Note that the model does not rely on any specific physical or chemical mechanism that is responsible for the disorder, which makes it a good candidate for explaining the ubiquitously observed behaviour.

One result of the field-dependent mobility is that the space charge limited current (SCLC, the maximum current that can flow in the bulk of the sample) does no longer follow a simple $V^2/L^3$ scaling\textsuperscript{124} on the voltage $V$ and sample thickness $L$. Murgatroyd\textsuperscript{125} was able to show that, for a mobility as in Eq. (3-9), the monopolar SCLC current could be well approximated by:

$$J = \frac{9}{8} e \varepsilon_0 \mu_0 V^2 \frac{1}{L^3} e^{-0.89 \frac{V}{\mu_0 L}}.$$

(3-10)

\textsuperscript{†} A similar morphology has been suggested for doped conducting polymers.\textsuperscript{121}
Chapter 4

Device Design and Characteristics

4.1 Introduction

The purpose of this diploma work has been the development of a switchable polymer-based diode. The chosen architecture for this device, as motivated in Section 4.2, is a modified version of a recently developed highly rectifying diode, where an intermediate layer, able to switch its internal resistance during operation, has been incorporated into the bottom contact layer structure. Its fabrication scheme can be found in Section 4.3. Note though, that machine errors and contact problems made the evaluation of a suitable process route for such a device structure difficult and it was not until the last day in the lab that the first indications of a switching behaviour were detected (see Section 4.4). Hence, several modifications might still be necessary to undertake in order to get the device to work properly (see Section 4.5).

4.2 Device Architecture and Design Motivations

Having already outlined the principal structure of the switchable diode, a brief motivation of its design might be in place. Basically, the layer architecture has been chosen in such a way as to mimic the elements and electrical behaviour of a circuit consisting of a switchable resistance in series with a rectifying diode (see Figure 4.1a), since the electrical characteristics of such a circuit can, by means of the variable resistance, be switched between an insulating and a rectifying behaviour (see Figure 4.1b). But even though being fairly simple in theory,

† Using a transparent bottom contact, i.e. glas/SiO₂/ITO, and a photochromic switching layer, able to shift its internal resistance upon exposure to light, this behaviour could be duplicated for light sensor applications.
the physical realisation of such a component proved to be a difficult task. Hence, a detailed account over the design choices in the architecture can be found below.

![Image of equivalent circuit and principle electrical characteristics](image)

**Figure 4.1** The (a) equivalent circuit of a switchable diode and its (b) principle electrical characteristics.

### 4.2.1 The Backbone Architecture: A Highly Rectifying Polymer-Based Diode

The framework of the architecture is, as previously mentioned, the highly rectifying hole-only diode structure recently developed by Stoltz et al.\(^{12}\) (see Figure 4.2). Even though its design has been developed by others, the design choices they made are briefly discussed below since they quite beautifully illustrates the complex nature of component development.

In general, in order to fabricate diodes with high rectification, based on semiconducting polymers, contact materials are required that allow efficient injection of holes\(^{†}\) into the polymer under forward bias, and much less so under reverse bias. Normally this is achieved using an anode metal with a work function value that match, or make a low potential barrier, to the ionisation potential (i.e. the HOMO-level) of the polymer. In reverse bias a cathode metal with a work function value close to the Fermi level of the pristine polymer (i.e. the middle of the band gap) assures high enough barriers for both electrons and holes to keep the current low, having thus as a result a high rectification ratio.

Since the semiconducting polymer chosen for the diode structure, poly(2-methoxy, 5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV), has an ionisation potential of 5.3 eV and a pristine Fermi level of 4.15 eV,\(^{127}\) the obvious choice of contact metals should be gold (5.1 eV)\(^{12}\) and aluminium (4.2 eV).\(^{12}\) However, polymer films spin coated on inert materials such as gold often show pinholes by dewetting.\(^{12}\) These are not acceptable, when an upper electrode is evaporated on top of the polymer in a sandwich geometry.

The solution to this problem is to introduce an intermediate polymer layer that stabilises the interface. It should also form a low potential barrier to the MEH-PPV HOMO-level, while preserving the metal conductivity of the contact, in order to preserve the functionality of the device. The best candidate displaying these characteristics was the conductive polymer blend of poly(3,4-ethylenedioxythiophen) (PEDOT) and poly(4-styrenesulfonate) (PSS), from here on referred to as PEDOT(PSS), with a work function value of 5.2 eV\(^{128}\) and a conductivity comparable to those of anisotropic metals (described by Eq. (2-7) and Eq. (2-8))\(^{‡}\). However, due to its high resistivity, unwanted voltage drops may occur under high currents, whereas the underlying metal layer was preserved in order to make high conductance lines.

Note that since no potential barriers form between the metallic compounds, the requirement of specific metal work function values are no longer applicable. Hence, the anode metal may bee chosen freely, and diodes made with several metals of varying work function values \([\text{Al(4.2 eV), Ag(4.3 eV), and Cu(4.5 eV)}]\) where thus tested by Stoltz et al.\(^{12}\) They concluded that in all cases, the current flow of holes that was contact limited changed to bulk

\(^{†}\) Due to an extensive trapping of electrons in the semiconducting polymer chosen for this diploma work, i.e. MEH-PPV,\(^{126}\) the current is mainly carried by holes.

\(^{‡}\) The morphology of PEDOT(PSS) is such that the PEDOT components tend to form clusters or grains with metallic conductivity, surrounded by insulating PSS species.\(^{129,130}\)
limited when PEDOT(PSS) was used in between the anode metal and the MEH-PPV layer. However, copper displayed both superior stability and ease of patterning, and was thus the natural choice of anode material.

![Layer architecture of the highly rectifying diode reproduced in this diploma work.](image)

**Figure 4.2** Layer architecture of the highly rectifying diode reproduced in this diploma work.

### 4.2.2 Design Modifications in order to Introduce Switching/Sensor Functionality into the diode device

As previously mentioned, in order to achieve the desirable switching functionality of the device designed for this diploma work, an intermediate layer capable of switching its internal resistance was incorporated in the Cu/PEDOT(PSS) anode contact. Such a material can be any kind of compound comprising updating, control or switching of internal resistance or change of conduction/valance band positions due to external stimuli of any kind. Such a material was tested.

### 4.3 Experimental

The process routes developed during this diploma work are presented below. For a more detailed description of the general fabrication techniques, e.g., spin casting and vacuum deposition, and processes, e.g., photolithography, the reader is referred to the excellent textbook by P. Van Zant.¹³¹

#### 4.3.1 Process Routs

The MEH-PPV based diodes were constructed in a sandwich geometry using Cu/PEDOT(PSS) as the anode and Al as the cathode. Briefly, 4-inch n-type silicon wafers (8-13 Ω·cm), <100> 300 μm thick) where covered with 1000 nm thick thermally grown oxide, and subsequently rinsed in water and annealed for 10 min at 100°C. The anode metal, copper (Cu), where then deposited onto the substrates by means of argon sputtering to a thickness of 150 nm. After subsequent patterning using standard photolithography processes (see Ref. 135), the structures where coated with a 230 nm thick PEDOT(PSS) (Baytron P, Bayer AG) layer, deposited through spinning techniques at 400 rpm from a 7 mg/ml chloroform solution.¹ Remaining water in the layer was removed by annealing treatment during 5 min at 120°C. Immediately thereafter, the MEH-PPV (poly(2-methoxy, 5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene), Aldrich) layer was spin casted, also at 400 rpm, from a 7 mg/ml chloroform solution to a thickness of 150 nm. Finally, the upper electrode, aluminium (Al),

¹ Previously filtered using 0.45 μm membrane filters.
² Note that due to the slow kinetics of the dilution process, it takes a couple of days to prepare a 7 mg/ml sample of MEH-PPV. In order to speed up this process, preheating the sample at 50°C in 30 min is recommended, as well as occasional stirring of the sample.
was vacuum evaporated at $1.6 \times 10^{-6}$ torr, using flat tungsten filament, through a contact shadow mask to a thickness of $31 \pm 1$ nm.

In order to incorporate the switching layer the process route of the rectifying polymer diode required a slight modification. Instead of the deposition of PEDOT(PSS) after patterning, the molecular layer was spin casted onto the wafer. In order to improve adhesion of PEDOT(PSS) to the molecular layer, remaining water was subsequently removed through annealing treatment for 2 min in 110°C.

4.3.2 Measurement Techniques
In order to measure surface layer profiles, e.g., layer thickness, and component electrical behaviour, i.e., current-voltage (I-V) characteristics, a DEKTAK$^3$ST surface profile measuring system and a HP 4155B semiconductor parameter analyser has been used, respectively. These are briefly discussed below.

The thickness of the spin casted layers have been established using a DEKTAK$^3$ST surface profile measuring system, their primary function being to measure film thickness by scanning step heights and trench depths. The fundamentals of stylus profiling are fairly straightforward. The system rely on a small diameter metal stylus that is linearly moved across the sample surface. As the stylus encounters surface features, it is forced to move vertically. This movement are transformed through a lever to a set of electromechanical transducers whose output signal, having undergone some signal processing, provides a varying DC signal proportional to the stylus displacement. This signal is then digitised and stored to represent the surface profile of the sample.

Using a HP 4155B semiconductor parameter analyser, the electrical characteristics of the device have been determined. Its working principle is quite simple. After the component has been electrically connected to the analyser via stylus probes, a voltage sweep is applied and the corresponding induced current output is determined with a resolution set by the number of data points and the signal integration time. Subsequently digitised and stored in the machine memory, the current may then be graphically displayed as a function of voltage, i.e., $I(V)$, on a small monitor on the machine. Note that good contact between the stylus probes and the device contacts, i.e., the aluminium and copper lines, is a requirement for accurate measurements. But even though the connection process was carefully monitored in a microscope, non-ideal contacts were formed.

4.4 Results and Discussion
Once developed and fabricated, the electrical characteristics of the two devices, i.e. the ‘replicated’ rectifying diode structure and the switchable polymer diode, was determined using a HP 4155B semiconductor parameter analyser (previously described in Section 4.3.2). These results are presented and discussed in the subsequent sub-sections.

---

$\dagger$ The high pressure is required for uniform coating as well as to avoid oxygen contamination of the sample, leading to the formation of a thin, insulating layer of aluminium trioxid ($\text{Al}_2\text{O}_3$).

$\ddagger$ For successful aluminium evaporation, the filament, i.e. the boat, should be fasten gently so as to avoid torsion of it. Additionally, the amount of pellets should be held at a minimum, since Al interacts with the tungsten material of the filament, making it fragile if great amounts of aluminium are used.

$\zeta$ The parameter settings required to assure repeatability are: Measure-range: 65 kA, Length: 1000 μm, Speed: Low, Profile: Hill-Valley, and Stylus Force: 3 mg. This assures a vertical resolution of 10 Å and a collection of data samples every 200 nm. Note that the low stylus force, i.e., pressure, is needed to avoid plastic or elastic deflection, even though this may cause the stylus to hop over large steps and features.$^{31}$
4.4.1 The Electrical Characteristics of the Rectifying Diode Structure

Much can be learnt about the anode/MEH-PPV/Al system by studying its ideal $J/V$ characteristics, obtained by Stolz et al.\textsuperscript{12} As can be seen from Figure 4.3, the $J/V$ characteristics with and without the PEDOT(PSS) layer are very different. The almost symmetric $J/V$ shape for the Cu anode (open circles) is converted to a diode behaviour after inclusion of the PEDOT(PSS) layer (solid circles). This is expected since the intermediate PEDOT(PSS) layer lowers the potential barrier for forward current injection over the anode/MEH-PPV-interface, from $\phi_{Bi} \approx 0.8$ eV for Cu/MEH-PPV to $\phi_{Bi} \approx 0.1$ eV for Cu/PEDOT(PSS)/MEH-PPV,\textsuperscript{13} rendering the $J/V$ characteristics asymmetric under reverse and forward bias. Additionally, the inclusion of the PEDOT(PSS) layer leads to a bulk limited current regime in the forward bias at high fields.

![Figure 4.3](image)

A qualitative understanding of the $J/V$ characteristics for the Cu/PEDOT(PSS)/MEH-PPV/Al system in Figure 4.3 is obtained with the help of the simplified energy level diagram in Figure 4.4. In the unbiased system, the difference in the work function values of the electrodes creates an inherent potential\textsuperscript{134} $V_{Bi} \equiv 1$ eV across the polymer layer that opposes hole injection over the PEDOT(PSS)/MEH-PPV interface (see Figure 4.4a). Applying an external positive bias will reduce the potential drop, but as long as the joint potential ($V_a - V_{Bi}$) is less than zero, that is in the range of $0<V_a<1$, the electric field within the polymer will oppose charge injection, and the forward drift current will be at the noise level of the equipment. Due to the limited charge flow, this region in the J(V) diagram is commonly referred to as the ‘ohmic’ region.

When the applied voltage exceeds $V_{Bi}$, i.e. $V_a - V_{Bi} > 0$, the polarity of the electric field across the organic layer is reversed so as to support charge injection over the low energy barrier at the PEDOT(PSS)/MEH-PPV interface, as displayed in Figure 4.4b. In accordance with CLC theory, applicable for $\phi_{Bi} < 0.3$ eV (see Section 3.4), the current should display an exponential behaviour for as long as the bulk is able to transport the injected holes. From Figure 4.3 it can be seen that such a contact limited current (CLC) region does exist in the region from 1 to 2 V, where the current increases five orders of magnitude. Beyond 2 V the current becomes space charge limited (SCL), i.e. dependent on the transport properties of the MEH-PPV layer.
At 3 V, a six orders of magnitude rectification can be deduced, increasing to seven orders between 4 and 8 V. After 8 V the injection of holes from Al to MEH-PPV during reverse biasing, i.e., \( V_{i} < V_{a} < V_{bi} \), increases the reverse current, and thus decreases the rectification value.

![Energy level diagram of the Cu/PEDOT(PSS)/MEH-PPV/Al system](image)

**Figure 4.4** Energy level diagram of the Cu/PEDOT(PSS)/MEH-PPV/Al system, where the active polymer material is depicted as a fully depleted semiconductor. (a) Upon contact an inherent potential is established and needs to be compensated for, (b) before the device will begin to operate.

Even though the better part of this diploma work was spent on trying to reproduce these results, non-of the fabricated structures displayed such excellent characteristics as those in Figure 4.3, presumably due to contact problems during electrical characterisation. In fact many component actually acted as short circuits. This was ascribed the possible penetration of the thin Al-conductance lines by the metal stylus. Hence, a silver paste was deposited onto the Al-contacts in order to release some of the stylus pressure during probing, and indeed the yield rate for the diodes improved significantly. However, due the possible incidence of unwanted interfacial layers (see Section 4.4.3) and the difficulties of assuring sufficiently good probe contact towards the Cu-conductance lines, only non-ideal characteristics was obtained. In fact, diodes fabricated using the process scheme in Section 4.3.1 never displayed better rectification ratios than \( \sim 10^{4} \) (see Figure 4.5).

![Semilog plot of the current-voltage characteristics of the best reproduction of the Cu/PEDOT(PSS)/MEH-PPV/Al -structure.](image)

**Figure 4.5** Semilog plot of the current-voltage characteristics of the best reproduction of the Cu/PEDOT(PSS)/MEH-PPV/Al -structure.

### 4.4.2 The Electrical Characteristics of the Switchable Polymer Diode

Having achieved a sufficiently high rectification ratio and by doing so also verified the principle functionality of the diode structure discussed above, a thick layer of the molecular material, able to switch its internal resistance and hence also its current throughput (as previously pointed out), was incorporated at the interface between copper and PEDOT(PSS).
As predicted, a bistable, electrically triggered, switching mechanism was detected, but it came, rather unexpected, at the cost of current rectification. Additionally, the differences in current levels are lower than expected only a factor 3. Both these anomalies might be caused by unintentionally introduced interfacial layers at the junctions towards copper and PEDOT(PSS), formed during device fabrication. This hypothesis has, however, neither been verified nor discarded, since the first and only electrical characterisation of the device was obtained at the last day in the lab.

4.4.3 Non-ideal Characteristics - Indications of Unwanted Interfacial layers?

As previously mentioned, the non-ideal characteristics of both the rectifying and the switchable/updateable polymer diodes may be caused by the possible incidence of interfacial layers, unintentionally introduced during device fabrication. In fact, according to Salaneck et al., such interfacial layers are highly unlikely not to occur. If sufficiently thick, these layers may very well account for the deteriorated characteristics of the rectifying diode and the extremely low rectification ratio of the switchable polymer diode, since they would alter the geometry of potential barriers across the junctions. Some possible layers are accounted for below. Note, though, that since the first and only successfully fabricated and electrical characterised switchable polymer diode was completed on the very last day in the lab, the presence of these films have been experimentally verified for the structure.

When the top electrode aluminium metal is vapour-deposited onto the surface of the conjugated polymer film, chemistry occurs and an interfacial layer is formed between the electrode metal and the bulk of the conjugated polymer film as the Al atoms form covalent bonds to the vinylene moiety of the monomers. This alters the bond alternation pattern of the conjugated system and somewhat reduces the π-conjugation. Additionally, if there are oxygen-containing species on the polymer surface, either in the form of chemical side groups or as impurity molecular species, the vinylene part is not the only preferred interaction unit, and a metal oxide interfacial layer may be formed, the detailed nature of which depends upon the specific nature of the oxygen-containing species.

Another imperfection within the structure might be introduced upon deposition of PEDOT(PSS) by spin coating as a phase segregation of PEDOT and PSS occurs, the end result of which is a thin film of PSS-molecules over the PEDOT layer. Being an insulating material, the PSS film would be unable to trap charges from the electrode, and may hence help in improving the carrier injection from PEDOT at low biases. The existence of the PSS film, though, have been questioned recently by Greczynski et al.

Additionally, the introduction of a sensor/switching material might give rise to unwanted interfacial films between included layers. Such interfacial layer can have bad impact on the overall device performance.

4.5 Further Development

In the nearby future two possible developments of the switchable-diode-concept may be undertaken, both of which involves alternations of the anode contact, i.e. the switching material/PEDOT:PSS structure.

4.5.1 Rebuilding the Switching Diode to Achieve Ideal Switching Characteristics

Since the electrical characteristics of the fabricated devices are far from ideal, an alternative structure, and hence also an alternative process route, ought to be evaluated. By postponing the bottom contact patterning and instead layer the entire wafer first with the sensor/switching material, and then with an additional layer of copper, if possible by means of argon sputtering,
the problems of possible interfacial chemistry between the switching material and subsequently deposited PEDOT(PSS) may be avoided. Note though that the contact layers still needs to be patterned and that a suitable photolithography process needs to be developed. Also, due to the height of the thereby formed conductance lines, \( \sim 1000 \) nm (see Section 4.3), a spacer ought to be used to fill in the gaps between the lines.

Such a component should, all other things preserved, be the exact physical realisation of the equivalent circuit displayed in Figure 4.1a, and may very well yield the desirable switching characteristics of Figure 4.1b.

### 4.5.2 Rebuilding the Anode Contact to Yield New Component Functionality

So far, only the electrical switching characteristics has been explored, since, as stated in Section 1.2, such a component may be of commercial interest in sensor, display, signal processing, detection technologies etc. However, other systems with other application areas may be designed by rebuilding the anode contact, and, in the case of photovoltaic, i.e. light detection, devices, replace the substrate with glass/SiO\(_2\) discs.\(^*\) For example, if an indium-tin-oxide layer is deposited onto a glass/SiO\(_2\) substrate and a material capable of switching its ability to reflect specific wavelengths of light subsequently is layered on top, such a structure might, at least in theory, be used as a shutter for sensor applications. Note that if the polymers used in this diploma work are kept, the top contact material should be a low work function metal, e.g., calcium, able to collect excitons, i.e., electrons, formed within the MEH-PPV bulk upon absorption of incoming light.

\(^*\) The SiO\(_2\) layer is required in order to block the diffusion of sodium from the glass into the ITO.\(^{139}\)
Appendix A

International System of Units (SI Units)

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
<th>Symbol</th>
<th>Dimension</th>
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</thead>
<tbody>
<tr>
<td>Length(^1)</td>
<td>Meter</td>
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</tr>
<tr>
<td>Mass</td>
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<td>Kg</td>
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<td>Light intensity</td>
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<td>Frequency</td>
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<td>Light flux</td>
<td>Lumen</td>
<td>Lm</td>
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\(^1\) It is more common in the semiconductor field to use cm for length and eV for energy (1 cm = 10\(^{-2}\) m, 1 eV = 1.6 \times 10\(^{-19}\) J).
# Appendix B

## Greek Alphabet

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