FULLY SOLUTION PROCESSED LOW TURN-ON ORGANIC P-N JUNCTION DIODES FOR RECTIFIER APPLICATION

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Dedication

I want to dedicate this work to my family for their constant encouragement and support to make this happen. Without their sacrifice, it would have been impossible to achieve this major professional accomplishment.
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Figure 4. 4 Schematic of the P-N junction diodes (inset) and the J–V characteristics for each diode. The active area is 0.25 mm^2 for all the diodes, the thickness of both N2200 and T3DPP are always 50 nm. T3DPP was doped by different doping method: sequential doping from 1 mg/ml F4TCNQ in CF and mixed solution doping from the T3DPP/15 wt% F4TCNQ in CF.

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Figure 5. 2 Rectifying signal of the diode under different input frequency. (Diode size: 0.25 mm^2, C_L=100 nF, R_L= 1 MΩ)
Abstract

Solution processed organic materials are an appealing opportunity for emerging electronic applications since they can enable the fabrication of large area and flexible electronics by means of cost-effective industrial manufacturing techniques. On the other hand, the solubility of the materials becomes an issue for the fabrication of vertical organic devices, e.g. vertical diodes, where several layers of organic materials have to be deposited one on top the other, without negatively affecting the electronic properties of underneath layers.

To this end, in this thesis work, the use of latent pigments, highly soluble molecules which can produce insoluble films after a post-deposition thermal cleavage of solubilizing groups, is introduced. Small molecule T3DPP was selected by applying this latent pigment strategy, which enabled the fabrication of a vertical junction diode with pristine layers, which finally showed high rectification ratio $10^3$, low turn-on voltage and ideality factor of 17.

Furthermore, the effect of two different doping methods was studied in order to enhance the high conductivity of the semiconductor. Then, the junction diodes doped semiconductors were fabricated. Unfortunately, the diodes lost the rectification behaviour, suggesting that further work is still necessary to optimize the process. Finally, the frequency response of the diodes to the AC signal were demonstrated, showing good rectifying behaviour up to 1 kHz AC signal input.
Introduction

Nowadays, organic devices are grabbing a tremendous technological and scientific interest due to possibility of merging remarkable architecture flexibility of organic materials with the well-established properties of inorganic compounds. This versatility has provided the space for fabrication of printable, low-cost, large-area and flexible electronic and optoelectronic devices such as FETs, light-emitting diodes, diodes as rectifier and in memory devices etc. for various applications.

However, an organic electronic device is typically composed by functional multi-layers that have to be deposited one on top of the other, which requires that the deposition of a new layer has no negative effects on the electronic properties of the underneath layers. One of the most exploited approaches to ensure this is to rely on orthogonal solvents, i.e. solvents that solubilize the compound being deposited but cannot solubilize the layers below. Obviously, especially in the case of multi-layers stacks, such approach poses stringent constraints on the processing solvents, complicating process flows and limiting the possible choices also in terms of materials. For such a reason, the so-called latent pigment strategy was introduced by Zambounis, where insoluble pigments are made soluble by functionalization with volatile solubilizing moieties which can then be cleaved through either a thermal or optical process, unlocking molecular interactions, such as hydrogen bonding and π-π interactions. Chemical protective groups, like the t-butoxycarbonyl radical (-tBoc), are meant to make the derivative soluble by hindering hydrogen bonds. One of the main advantage of this approach is the possibility to remove the -tBoc radical in a
post-processing step by thermal treatment after film deposition.

By applying this latent pigment strategy, organic molecules T3DPP and N2200 were selected, which enabled the fabrication of a vertical junction diode with pristine layers, which finally showed high rectification ratio $10^3$, low turn-on voltage and ideality factor of 17.

With the intention of obtaining high conductivity of the semiconductors, two different doping methods, mixed solution and sequential doping methods, were developed. Fortunately, high conductivities were obtained for both T3DPP by sequential doping method, and N2200 by mixed solution doping method.

Finally, the frequency response for the fabricated diodes was also studied, where the diodes showed good rectifying behaviour up to 1 kHz AC signal input.

This thesis work, lasted about nine months, was performed at the Center for Nano Science and Technology@PoliMi (CNST), of the Istituto Italiano di Tecnologia (IIT) under the supervision of Mario Caironi, tenure track researcher and Doctor Michele Girogio at CNST, and Chiara Bertarelli, researcher at Politecnico di Milano.
Chapter 1

You can know the name of a bird in all the languages of the world, but when you’re finished, you’ll know absolutely nothing whatever about the bird... So let’s look at the bird and see what it’s doing - that’s what counts.

Richard Feynman

State-of-the-art

In this chapter, the typical characteristics that make organic semiconductors suitable for organic electronic applications are briefly introduced, and their electronic properties are described as well. Furthermore, a brief structural and functional description of organic diodes and Bipolar junction transistor are presented.

1.1 Organic semiconductors

Organic semiconductors can be broadly classified into two categories: small molecules or oligomers (usually processed in vacuum) and polymers (usually processed by wet chemical techniques). The term “organic” always refer to the large pool of carbon-based compounds, which mainly composed by significant amount of C-H or C-C bonds. However, this definition is somewhat arbitrary, which excludes
some compounds historically classified as organic (e.g. H₂CO₃).

Few decades ago, it was believed that only metals and inorganic composites could conduct electricity, while organic molecules were believed to be insulators because of relatively large distances within intermolecular and lack of suitable charge carriers. In 1954, it was reported firstly that bromine-doped perylene (I-1) was electrically conductive.\(^1\) However, most scientists thought the conductivity was attributed to the bromine rather than the perylene. After 10 years, iodine doped polypyrrole (I-2) was reported as an electrically conductor with a conductivity of 1 S/cm.\(^2\) Nevertheless, little attention was paid to this discovery at that time. It was not before 1972 that people started to believe in this phenomenon, when the group of Alan J. Heeger published the conductivity of a fully organic charge-transfer complex which composed of N-methyl-phenazine (NMP) and tetracyanoquinodimethane (TCNQ) (I-4).\(^3\) One year later, the same group discovered superconductivity in a charge-transfer complex of tetrathiafulvalene (TTF) and TCNQ (I-5).\(^4\) The first organic semiconductor was discovered by McGinness et. al. in 1974.\(^5\) In 1977, Shirakawa, MacDiarmid and Heeger reported electrical conductivity in iodine-doped polyyacetylene (I-3).\(^6,7\) For this discovery they received the Nobel Prize for Chemistry in 2000.

Over the past decades, Organic electronics have shown incredible expansion driven by innovative products. Many new organic (semi-)conductors have been developed and incorporated into devices, such as transistors,\(^8\) diodes,\(^9,10,11\) solar cells,\(^12\) and sensors\(^13\) due to its obvious advantages, such as light weight, mechanical flexibility, possible chemical modifications, and cheap processing (e.g. ink-jet printing, spin
coating). However, it still needs large improvement in low carrier mobility, and stability with respect to inorganic electronics, which is also the main obstacle to take place of the inorganic electronics in commercial industrial.

![Chemical structure of some conductive materials](image)

1.2 Molecular Orbitals Theory

Let us begin by considering the formation of a small molecule constituting of a number of atoms. Molecular orbital (MO) theory, developed in the course of modern chemistry, is a method for determining a given molecular structure. There, unlike in valence bond theory, electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. The total number of orbitals is conserved; i.e., the number of MOs equals the number of original atomic orbitals. The theory asserts that atomic orbitals no longer hold significant meaning after atoms form a molecule, and that electrons no longer belong to any particular atom but to the molecule as a whole.
MO theory was initially considered as a competitor to valence bond theory before it was realized that the two methods are closely related, and by an extension of the concepts, they eventually become equivalent.

1.2.1 Hybridizations

Carbon atoms have six electrons, electronic configuration of unbounded carbon atoms is $1s^22s^22p^2$. Nevertheless, bounded carbon atoms, e.g. carbon atoms in polymers, change their electronic configuration by a mechanism called hybridization, which is described in the following sections.

![Figure 1.2 Representation of p and s orbitals of unbound carbon atom.](image)

$sp^3$ hybridization

The $sp^3$ hybridization tends to occur when an $s$ orbital (2s) and three $p$ orbitals ($2p_x$, $2p_y$, $2p_z$) combine forming four new orbitals energetically equivalent one to each other, but different from the original ones; these new orbitals forms a new chemical, stable geometry, where the nucleus reside at the centre and new four C-H bonds are directed to the four vertexes of a tetrahedron.

When carbon involves $sp^3$ hybridization, it generate four single $\sigma$-bonds, where a carbon’s electron is shared in a covalent bond in each formed hybrid orbital.
Figure 1. 3 a) Four sp3 orbitals directed as the vertexes of a tetrahedron. b) An example of sp3 hybridization in a molecule (methane) where a carbon bounds into four hydrogen atoms.

\textit{sp}^2 \text{ hybridization}

The \textit{sp}^2 hybridized orbitals could be formed when a 2s orbital and two 2p orbitals hybridize, resulting in the formation of three iso-energetic new orbitals. The remaining p orbital, which doesn’t participate in the hybridization, is perpendicular to plane. These new orbitals are separated by an angle of 120° each other. What’s more, in this case, hybrid orbitals form \(\sigma\)-bonds with other atoms, while the remaining p orbitals form another kind of bond, so-called \(\pi\)-bond, which is distinguished by its symmetry from \(\sigma\) one. Electrons bonding energy is weaker in these \(\pi\)-bonds. For this reason these electrons are delocalized and are responsible for the electronic conductivity.

\textit{sp} \text{ hybridization}

In this case, the 2s and one of the 2p orbitals combine, creating two new orbitals separated by 180°. Joining two atoms in such a configuration gives rise to a \(\sigma\) and two \(\pi\)-bonds, creating a triple bond between the atoms. These two \(\pi\)-bonds make
the new formed molecules highly active, compared to previous two hybridizations.

Figure 1. 4 a) sp² orbitals are on the xy plane perpendicular to the axis of the not-hybridized 2pz orbital, and are separated by a 120° angle. b) When two molecules with a carbon sp² form a bond C-C, a σ-bond occurs between sp² orbitals, and a π-bond forms between sp² orbitals, and a π-bond forms between the p orbitals.

Figure 1. 5 a) Sp orbitals have the same axis of the used 2p orbital. b) After the formation of a bond between two sp carbons, one σ-bond occurs due to hybridized orbitals and two π-bonds form between the not-hybridized p orbitals.

1.2.2 Linear Combination of Atomic Orbital

The linear combination of atomic orbitals (LCAO) is a quantum superposition of
atomic orbitals and a technique for calculating molecular orbitals in quantum chemistry. LCAO does not give exact solutions to the Schrödinger equation, but provides approximate solutions. Several approximations and simplifications are required before LCAO to determine electronic energies in MOs. The first approximation can be made assuming that electrons can move much faster than nuclei: the Born-Oppenheimer approximation. We can therefore treat the nuclear and electronic motions independently. By neglecting the nuclear kinetic energy, the electronic Hamiltonian for solving the Schrödinger equation has a simple form.

The next approximation is known as the independent electron model. Assuming each electron to move in an average potential, which incorporates the interactions with the nuclei and an averaged interaction with the other electrons, the electronic Hamiltonian can be separated into individual parts:

\[ \hat{H} = \hat{H}_1 + \hat{H}_2 + \cdots \]

where \( \hat{H}_i \) is dependent only on the properties of each electron. The total electronic energy is then given by: \( E = \varepsilon_1 + \varepsilon_2 + \cdots \), i.e., by the sum of energies of the individual molecular orbital occupied with an electron. The problem is then reduced to an one-electron Schrödinger equation:

\[ \hat{H}_i \Psi_i = \varepsilon_i \Psi_i \]

where \( \Psi_i \) is the one-electron wavefunction of a molecular orbital.

The final approximation is made by the LCAO method. This method supposes that we

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1In quantum chemistry and molecular physics, the Born-Oppenheimer (BO) approximation is the assumption that the motion of atomic nuclei and electrons in a molecule can be separated. The approach is named after Max Born and J. Robert Oppenheimer. In mathematical terms, it allows the wavefunction of a molecule to be broken into its electronic and nuclear (vibrational, rotational) components: \( \Psi_{\text{total}} = \phi_{\text{electronic}} \times \phi_{\text{nuclear}} \). Computation of the energy and the wavefunction of an average-size molecule is simplified by the approximation.
can construct a MO by linear superposition of atomic orbitals centered on individual atoms as

$$\psi_i = \sum_{j=1}^{n} (C_{ij} \Phi_j)$$

where $\Phi_j$ is an atomic orbital. The coefficients $C_{ij}$ may be determined numerically, e.g., by insertion of this equation into the Schrödinger equation above and by application of a variational principle such as the Hartree-Fock method.

### 1.2.3 Energy Splittings

The linear combination of wavefunctions results in two types of solutions: symmetric and antisymmetric functions. An equal number of bonding orbitals and antibonding orbitals are thus formed. The splitting of energies between the two different types of orbitals generally depends on the degree of overlap of the atomic orbitals. For a qualitative understanding, we can consider two distinct atoms each having one electron: Let us now take the simplest case of homonuclear molecules, such as diatomic (H$_2$, He$_2$, O$_2$, ...) or ethylene (C$_2$H$_4$) molecules. As the atoms are brought together, their orbitals overlap, and the increasing Coulomb interaction between the atom cores and the electron splits the orbital energy levels.

The eigenvalue of an LCAO orbital, $\psi = c_1 \Phi_1 + c_2 \Phi_2$, is given by

$$\varepsilon = \frac{c_1^2 \beta_1 + 2c_1c_2 \gamma_{12} + c_2^2 \beta_2}{c_1^2 + c_2^2 + 2c_1c_2 S}$$

leading to nontrivial solutions for the energy

$$\varepsilon = (\beta + \gamma)/(1 + S) \quad \text{bonding}$$

$$\varepsilon^* = (\beta - \gamma)/(1 - S) \quad \text{antibonding}$$
where $\beta_j$ (for a homonuclear molecule, $\beta = \beta_1 = \beta_2$) is known as the Coulomb integral which equals the energy of an electron in the corresponding atomic orbital $j$ in the molecular environment. $\gamma_{jk}$ ($\gamma = \gamma_{12}$) is the resonance integral which is a measure of the strength of bonding interaction as a result of overlap of the orbital $j$ and $k$. $S$ represents the overlap integral which is a measure of the effectiveness of overlap of the orbitals.

The bonding orbital is bonding in the sense that it is lower in energy than its constituent atomic orbitals. Neglecting the overlap integral $S$, the splitting between the bonding and antibonding orbitals is approximately $2\beta$. The number of split MOs is equal to the number of contributing atomic orbitals. Figure 1.6 shows a schematic of evolution of the energy levels for the simplest case.

![Energy Levels Diagram](image)

*Figure 1.6 Evolution of the energy levels of an aromatic molecule with an LCAO approach.*

### 1.2.4 Koopmans\' Theorem

The orbital energies $\varepsilon_i$ resulting from quantum-mechanical calculations can be associated with measurable quantities by means of Koopmans\' theorem:

1) The energy of an occupied orbital in $\psi_i$ is equal to minus the ionization
potential \((IP)\) for the orbital, i.e., to the amount of energy needed to bring an
electron onto the orbital from the vacuum level;

2) The energy of a virtual orbital in \(\psi_i\) is equal to minus the electron affinity \((EA)\)
for the orbital, i.e., to minus the amount of energy gained when an electron is
brought from infinity and added to the molecule.

Usually, the terms ionization potential and electron affinity refer to \(IP_1\) and \(EA_1\), that
is, the lowest \(IP\) and the highest \(EA\) for the molecule. The applicability of Koopmans’
theorem to real molecules is based on some assumptions that are only
approximately valid. It neglects the following effects:

1) The reorganization energy of the electrons in the ion;

2) The difference between the correlation energy of the neutral molecule and that
of the ion.

The first point is due to the fact that a charge distribution of the residing electrons
gives rise to an effective potential for each particular electron. If an electron is then
removed, this effective potential is naturally altered. The second point is due to the
tendency towards mutual avoidance by electrons of the same spin. Indeed, the
correlation energy is generally neglected in the first and second order approximation
of the variational method. Koopmans’ theorem states that these alterations are
small. Despite the limited accuracy, the terms “\textit{highest occupied molecular orbital}
(HOMO)” and “\textit{lowest unoccupied molecular orbital (LUMO)}” are commonly used by
convention to refer to \(IP\) and \(EA\), respectively.
1.3 Self-Polarization in Organic Solids

When organic molecules condense to form a solid state, the molecular features tend to retain their individuality, i.e., the electronic structure of a molecule changes only slightly due to weak intermolecular interaction of van der Waals type. Therefore, organic solids differ considerably in their mechanical, optical, and electronic properties from covalent or ionic crystals with a strongly bonded rigid atomic or ionic lattice characterized by complete loss of individual properties of the atomic particles. On the other hand, the energy relaxation caused by the displacement of dipole moments existing in a lattice environment is not negligible, especially for highly polarizable organic compounds such as aromatic and heterocyclic molecules. From these aspects, the LCAO eigenvalues calculated for an isolated molecule are actually
not valid for the molecules in the condensed matter.

Spectroscopic measurements reveal that the ionization potential of an anthracene crystal is by about 1.5 eV lower than that of an isolated molecule;\textsuperscript{[14]} i.e., the ionization of a solid requires less energy than that of a molecular gas. This can be attributed to the energy gain $P_h$ caused by the electronic polarization of the solid during the ionization process. The evolution of a valence level $E_h$ in a organic solid due to the effect of self-polarization is schematically indicated in Figure 1.8. Similarly, the electron affinity $E_{A_S}$ of a solid can be defined approximately by the sum of the electron affinity $E_{A_G}$ of a molecule and the electronic polarization $P_e$ of the surrounding molecules, leading to a conduction level $E_e$. Thus, self-energies $E_h$ and $E_e$ are of those quasi charge particles determined by many-electron interactions within the solid state, and the energy levels differ from the HOMO and LUMO for an isolated molecule. Nevertheless, we will use in this thesis by convention the terms “HOMO” and “LUMO” to refer to those levels in organic solids.

![Figure 1.8 Schematic energy diagram of isolated and solid states of an organic molecule. $IP_G$ and $EA_G$ refer to the ionization potential and electron affinity, respectively, in the isolated state. $IP_S$ and $EA_S$ are those in the solid state.](image)
1.4 Charge Transport

Conjugated polymers can be used as semiconductors in their undoped state. In addition, their electric conductivity can be improved with the doping process, analogously with inorganic semiconductors. Their doping processes are, however, quite different. Inorganic semiconductors are doped by introducing certain impurity atoms into the crystal lattice of the host material. In contrast, conjugated polymers are typically doped with an oxidation process, where the polymer chains become charged. The doping can be accomplished with electrochemical oxidation and chemical oxidation (i.e. with the use of oxidants) processes. Counter ions will transfer from the reaction medium (e.g. electrolyte) into the polymer matrix to maintain electro neutrality.

Typically, the charge transport and doping in conjugated polymers is explained with the Bipolaron model.[15] According to this model, charging of the conjugated molecules’ chains will create radical cations which are accompanied by lattice distortions. Such a radical cation along with its lattice distortions can be defined as a phonon-electron coupling, also called a polaron. A polaron will turn into a dication, which called bipolaron with further oxidation. These quasi-particles act as the charge carriers in the conjugated molecules. The formation of polaron and bipolaron by oxidation of chains is depicted for Poly-Para-Phenylene (PPP) in Figure 1.9. In place of oxidative doping, electron injection between a conducting polymer and an electrode causes similar charging of the polymer chains.

---

2 Polarons are quasi-articles associated to the movement of an electron within a material in which atoms are shifted by their equilibrium position to screen the electron charge. To be able to move the electron has to travel with the deformation itself and that deformation is seen as a phonon cloud.
The polarons and bipolarons are usually quite localized in the polymer chains. Conducting polymers are typically classified as disordered semiconductors, due to the presence of much energetic disorder.\textsuperscript{[16]} The disorder originates e.g. from their amorphous or semi-crystalline structure, \( sp^3 \) defects in the chain and chemical impurities. The disorder is a hindrance for the delocalization of the charge carriers along the whole chains. While in the case of inorganic crystalline semiconductors, the periodic long range order leads to efficient delocalization of charge carriers.\textsuperscript{[17]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{polaron_bipolaron}
\caption{Formation of the polaron and bipolaron states in PPP. In polyaromatic molecules, the radical cations and dications change the structure into a quinoid form.}
\end{figure}

For organic semiconductors, the charge transport along the polymer chains and also between the different molecules needs to be distinguished. As stated before, charge carriers can move relatively easily when the chains are long and defect-free, and the conductivity along the chains can be very high. The rate determining step is usually the inter-chain conductivity. Because of the localization of the charge carriers, the conductivity is typically thought to occur by phonon-assisted \textit{hopping} and \textit{tunnelling} processes.\textsuperscript{[18]} The hopping mechanism is dominant at room temperature.\textsuperscript{[19]} The conductivity increases with temperature, because of the thermal activation of the hopping process. However, the temperature dependency is largely dependent on the
doping level of the organic semiconductors: a organic semiconductors can show metallic conductivity (i.e. conductivity rises as temperature lowers) at high doping levels. While it is limited once considering the charge movements between different molecule chains. In this case, the charge have to overcome the energy barriers in order to move from molecule to molecule.

In general, polaron creates a new energy state between HOMO and LUMO gap, which also change energetic levels of the molecule and taking the name of intra-gap state. If several polarons interact among them, they can transform the isolated intra-gap states in polaronic bands, giving a conductive behaviour at the material.

The charge mobility in an organic solid state is determined by their ease degree of movement from molecule to its neighbour, and this movement usually happens through “hops” between the adjacent states. In the particular case of disordered structures, which is the situation considered in this thesis, a disperse of the density of states is generated, determining a misalignment of the energies of initial and final charge sites, so that the carriers have to overcome both spatial and energetic barriers.

Quantum tunnelling is the process that allows to overcome the spatial barrier and energy difference between the initial and the final states is provided by thermal energy. This tunnelling is known as thermally activated tunneling, and the probability of a charge hopping from one state to the other is given by the product:

\[
P_{\text{hopping}} \propto \exp\left(\frac{-\Delta E}{kT}\right) \exp\{-\alpha x\}
\]

3 Electrical mobility is the ability of a charge to move along a medium when it’s pulled from an electric field, it is defined as \( \mu = \frac{v_d}{E} \) where \( v_d \) is the drift velocity and \( E \) the electric field, a common unit used to represent it is \( cm^2/Vs \).
Figure 1. 10 a) Representation of a polaron, a charge that stay enough time in a localized state polarizes the atoms around it displacing them from their equilibrium position. b) Schematic depiction of the movement from a localized state to another, distance barrier is represented by $x$ and energetic one by $\Delta E$.

This equation highlights one major feature in organic crystalline semiconductors: the phonon activity and molecular vibration are improved as the temperature increases in organic disordered solids, which makes hopping become more likely, and charge mobility is enhanced as well. In contrast, in inorganic crystalline devices, the temperature rise results in increasing of scattering phenomena and mobility is reduced, and therefore the mobility, is enhanced if the hopping distances are shorter, which could be the case for highly ordered molecular structures. Starting from the early 80s, when the first organic transistors were demonstrated, there has been growing research effort towards the improvement of the semiconducting and conducting properties of organic materials for electronic devices manufacturing. In Figure 1.11 the increase of performance (in terms of carrier mobility) of organic semiconductors from 1980 up to 2010 is shown.$^{[21]}$
Figure 1. 11 Field effect mobility improvement for some categories of organic semiconductors, from the 80s to present.

1.5  P-N Junction Diode

The invention of the P-N junction is usually attributed to American physicist Russell Ohl of Bell Laboratories. However, Vadim Lashkaryov reported discovery of P-N junctions in Cu$_2$O and silver sulphide photocells and selenium rectifiers in 1941. A P-N junction is the simplest form of the diode, which behaves as ideally short circuit when in forward biased and behaves as ideally open circuit in the reverse biased. The name diode is derived from “di-ode” which means a device having two electrodes.

1.5.1  Working principle

When N- and P-type semiconductors are put in contact, free electrons in the N-side and free holes in the P-side begin to diffuse to the other side, leading to
recombination of these carriers at the interface region. The region close to the interface is called *depletion region*, because it is depleted of free carriers. On the N-side of a silicon P-N junction, the positively charged ions are $P^+$ ions and on the P-side the negatively charged ions are $N$. The presence of these uncompensated electrical charges creates a so-called built-in electric field. This built-in electric field, which is created in the depletion region by the different polarity of the fixed ions, gives rise to a drift current. In fact, if free electrons in the $P$-type region, moving by Brownian motion, end up in the edge of the depleted region, they will sense the electric field and will flow towards the $N$-type region and vice versa. On the other hand, the concentration gradient of electrons and holes, however, tends to move them in the opposite direction by diffusion. At thermal equilibrium, the flux of mobile carriers is zero because the field-driven migration flux is equal and opposite to the concentration-driven diffusion flux.

For an inorganic diode, the width of the depletion layer ($\omega$) can be derived from the Poisson equation, eventually we obtain

$$
\omega \approx \left[ \frac{2\varepsilon_r \varepsilon_0}{q} \left( \frac{N_A + N_D}{N_A N_D} \right) (V_{bi} - V) \right]^{\frac{1}{2}}$

where $\varepsilon_r$ is the relative dielectric permittivity of the semiconductor, $q$ is the elementary charge, $N_A$ and $N_D$ are the number of ionized donors and acceptors, $V_{bi}$ is the built-in voltage, and $V$ is the applied bias. The depletion region is not symmetrically split between the $N$ and $P$ regions, it will tend towards the lightly doped side. And depletion region is the only place where the electric field is nonzero, and the only place where the bands bend. Elsewhere in the semiconductor the field
is zero and the bands are flat. Inside of this $P$-$N$ junction, the Fermi energy, $E_F$, is halfway between the valence band (VB), and the conduction band (CB), if the semiconductor is intrinsic ($n = p$, where $n$ and $p$ are the number of free electrons and holes.).

Figure 1. 12 When $P$-type and $N$-type semiconductors are joined, electrons and holes recombine at the interface, leaving a depletion region that contains positively and negatively charged donor and acceptor atoms, respectively. At equilibrium, the Fermi level ($E_F$) is uniform throughout the junction. $E_F$ lies just above the valence band on the $P$-type side of the junction and just below the conduction band on the $N$-type side.

Figure 1. 13 Schematic representation of the three different working conditions of silicon $P$-$N$ junction diodes and its $I$-$V$ characteristics.

---

4 The Fermi energy is a concept in quantum mechanics usually referring to the energy difference between the highest and lowest occupied single-particle states in a quantum system of non-interacting fermions at absolute zero temperature. In a doped semiconductors, $P$-type and $N$-type, the Fermi level is shifted by the impurities, illustrated by their band gaps.
By applying a voltage, we can distinguish two zones of operation: forward bias and reverse bias.

**Forward Bias**

In forward bias, positive terminal of the battery is connected to the $P$-type material and negative terminal is connected to the $N$-type material so that holes are injected into the $P$-type material and electrons into the $N$-type material. The electrons in the $N$-type material are called *majority carriers* on that side, while electrons in the $P$-type side are called *minority carriers*. The same descriptors apply to holes: they are *majority carriers* on the $P$-type side, and *minority carriers* on the $N$-type side.

A forward bias lowers the built-in energy barrier. As shown in the figure 1.14, the step in band edges is reduced by the applied voltage to $\varphi_i - V_a$. The reduced step in band edges provokes an increase of the diffusion current, while the drift current stays approximately constant. In this case, a large net current flows across the device.

Under forward bias, the Fermi level cannot remain flat throughout the device as it is at equilibrium, but electrons and holes, *quasi-Fermi levels*, which have different positions. As shown in the figure, the electron quasi-Fermi level shifts with position, from the half-occupancy equilibrium Fermi level in the $N$-side, to the half-occupancy equilibrium level for holes deep in the $P$-side. The hole quasi-Fermi level does the reverse. The two quasi-Fermi levels do not coincide except deep in the bulk materials.

**Reverse Bias**

In the reverse bias condition, positive terminal of the battery is connected to the $N$-type material and negative terminal is connected to the $P$-type material so
that holes are injected into the $N$-type material and electrons into the $P$-type material. The occupancy level for holes again tends to stay at the level of the bulk $P$-type semiconductor while the occupancy level for electrons follows that for the bulk $N$-type. In this case, the $P$-type bulk band edges are raised relative to the $N$-type bulk by the reverse bias $V_a$, so the two bulk occupancy levels are separated again by an energy determined by the applied voltage. By applying a reverse bias, the built-in barrier is increased. As shown in the diagram, the step in band edges is increased to $\varphi_i + V_a$, and the depletion region widens as holes are pulled away from it on the $P$-side and electrons on the $N$-side. Thus, any current that flows is due to the very weak process of carrier generation inside the depletion region due to *generation-recombination defects* in this region. That very small current is the source of the leakage current under reverse bias. When the reverse bias becomes very large, reaching the breakdown voltage, the generation process in the depletion region accelerates leading to an *avalanche* condition which can cause runaway and destroy the diode.

![Energy band diagram of a P-N junction under thermal equilibrium (zero bias), reverse and forward bias.](image)

*Figure 1. 14 Energy band diagram of a P-N junction under thermal equilibrium (zero bias), reverse and forward bias.*
1.6 Space Charge Limited Current Models

This part starts with the brief discussion of space charge limited current models. Firstly, the typical metal-organic interfaces and contacts limit charge injection and transport will be discussed. Later on the Child’s Law, Mott-Gurney space charge limited current model, and trapped space charge limited current model. 

1.6.1 Metal-organic interfaces

Metal-organic interface plays a vital role to characterize the electrical behaviour of organic electronic devices. Figure 1.15 demonstrates the differences between typical metal-vacuum and metal-polymer interface energy band diagrams for further discussion. Apparently both energy band diagrams look same, but actually different charge injection mechanism is observed in both cases. The Fermi energy level of metal coincides with $E_f$ of vacuum or a polymer. But the barrier height between $E_f$ of metal and vacuum energy level for metal-vacuum interface is very high as compared to the barrier height between $E_f$ of metal and polymer interface. The barrier height difference between metal $E_f$ and vacuum level is defined as metal work function.\[^{22}\]

On the basis of these facts, Mott and Gurneys proposed metal-insulator barrier height reduction theory and justified the low metal-insulator barrier height as compared to the metal work function, which causes space charge limited current in insulating materials.\[^{23}\] It is unanimously accepted that Mott and Gurney’s proposed space charge limited current is also valid for most of insulating, semiconducting, and even conducting polymers.\[^{24}\]
1.6.2 Bulk-limited and injection-limited current flow

The limitation of current by an organic semiconductor can be classified as either (i) injection-limited or (ii) bulk-limited current flow. For injection-limited, the limitation of current through organic semiconductor is imposed by non-Ohmic metal-organic semiconductor interfaces, while for bulk-limited, the limitation is imposed by the bulk properties of organic semiconductor. If organic semiconductor is sandwiched between two electrodes and anyone electrode offers low barrier height (∼Ohmic contact) to the metal-organic semiconductor interface then the injected carriers from electrode from a space charge region consisting of a large number of injected carriers and equilibrium free carriers inside organic semiconductor. Since the mobility of carriers is very low with respect to inorganic semiconductors, therefore,
before traversing of injected carriers from one to the other electrode, more and more charges are injected. When an external electric field is applied, further charges are injected from low-barrier electrode to the organic semiconductor, and an equilibrium stage is reached when injected carriers are comparable or even higher than the free carriers concentration; at this stage, the flow of current is referred as \textit{space charge limited current} (SCLC).\textsuperscript{[24, 25]}

\textbf{Langmuir-Child space charge model}

Space charge limited current is a hot topic of research due to their great application for conducting/semiconducting materials. The origin of space charge theory was founded by C.D. Child and I. Langmuir from 1911 to 1913, when they reported the derivation of space charge limited current in a parallel-plane vacuum diode as\textsuperscript{[26, 27]}

\[ J = \frac{4\varepsilon_0}{9} \sqrt{\frac{2eV^3}{m_eL^2}} \]

where \(J\) is space charge limited current for vacuum diode, the \(\varepsilon_0\) is the vacuum permittivity, \(e\) is the coulomb charge of electron, \(m_e\) is the mass of electron and \(L\) is the vacuum spacing between the two electrodes, \(V\) is the applied voltage. The above equation is so-called Langmuir-Child law or three-halves power law. From the equation, it is clear that the space charge current is directly proportional to the three-halves power of the applied voltage and inversely proportional to the square of the displacement between electrodes.

\textbf{Mott-Gurney space charge model}

Apparently, Langmuir-Child space charge equation did not find any application for insulator or semiconducting materials due to the presence of vacuum and hence no scattering between electrodes. Therefore, Mott-Gurney proposed another SCLC
equation for organic semiconductor diode, which is similar to the Langmuir-Child equation with the following assumptions\cite{23}: (i) Active layer is trap-free for charge injection. (ii) Diffusion of carrier is negligible in active layer. (iii) Electric field at the injecting electrode is zero. Finally, solving the Poisson’s equation, which yields merely 9/8 for the deviation factor, leading to an ideal SCLC current density

\[ J \approx (9/8)\epsilon\mu \frac{V^2}{L^3} \]

where \( \mu \) is the carrier mobility in the organic semiconductor, the \( \epsilon \) is the vacuum permittivity. It is important to note that logarithmic graph (\( \log(J) - \log(V) \)) of equation above yields a straight line with a slope 2, which shows trap-free SCLC behaviour of polymer between electrodes as shown in Figure 1.16. There are only two regions, one is Ohmic region and other is space charge region and both regions can be distinguished by the order of slope. The transition between Ohmic and space charge regions takes place at specific voltage termed as threshold voltage \( V_T \). Furthermore, there is direct transition is observed from Ohmic to space charge limited region, which is not true in the presence of traps distribution inside organic semiconductor.

---

*Figure 1.16 (a) Space charge-limited current behaviour for organic semiconductor with only Ohmic and trap-free space charge-limited current regions. (b) Typical space charge-limited current*
behaviour for organic semiconductor. Four different charge-transport regions are clearly observed
(i) Ohmic region \((J \propto V)\), (ii) Trap-SCLC region \((J \propto V^3)\), (iii) Trap free voltage limited \(V_{TFL}\) region
\((J \propto d^2N_t)\), and (iv) SCLC region \((J \propto V^2)\).

**Trapped space charge model**

Generally speaking, an intermediate region is also observed between Ohmic and space charge limited region, and this region is called as *trapped space charge region*. The charge transport inside organic semiconductor within this region is mainly controlled by the trapping and de-trapping of carriers at both energetic and positional distribution. Traps are nothing just as impurities and/or structural defects, which provide localized states between HOMO and LUMO energy band gap of organic semiconductor. These trap sites could trap free carriers, leading to an overall decrease in electrical performances.\(^{[28]}\) When applied voltage is higher than the average energy associated with traps density, then organic semiconductor behaves trap-free space charge limited current as shown in the figure 1.16b.\(^{[29]}\)

### 1.7 Ideality factor of a diode

Here we could apply the typical forward bias current density \((J)\) relation for “inorganic” diodes,\(^{[58]}\)

\[
J = AT^2 \exp \left( \frac{-q\Phi_{bi}}{kT} \right) \exp \left( \frac{qV}{nkT} \right)
\]

Where \(A, T, q, \Phi_{bi}, k, V,\) and \(n\) are the Richardson constant, absolute temperature, electron charge, built-in potential, the Boltzmann constant, bias voltage, and ideality factor, respectively. The ideality factor is used to determine if a diode follows the ideal diode equation shown above. If there were no defects present, the total diode current would be a diffusion current and \(n\) would be 1. This would be the “ideal”
diode case. Otherwise $n$ is greater than 2, which is the “non-ideal” case.

Taking natural log for both sides of the equation gives,

$$\ln(j) = \ln\left[AT^2\exp\left(-\frac{q\Phi_{bi}}{kT}\right)\exp\left(\frac{qV}{nkT}\right)\right]$$

Rearranging terms on the right hand side gives,

$$\ln(j) = \frac{qV}{nkT} + \ln(AT^2) - \frac{q\Phi_{bi}}{kT}$$

Since the last two terms on the right hand side is constant ($C$), the slope from the experimental result gives the ideality factor ($n$) from the following relation.

$$\ln(j) = \left(\frac{qV}{nkT}\right) V + C$$

$$n = \frac{\Delta V}{\Delta \ln(j)} \frac{qV}{kT}$$

1.8 Bipolar Junction Transistor

The transistor is the main building block “element” of electronics. It is a semiconductor device and it comes in two main types: the Bipolar Junction Transistor (BJT) and the Field Effect Transistor (FET). Here we will describe the system characteristics of the BJT configuration and its working principles.

1.8.1 Device Configuration

The BJT is a three terminal device and it comes in two different types: the NPN BJT and the PNP BJT. The BJT is fabricated with three separately doped regions. In an NPN transistor, a thin and lightly doped $P$-type base is sandwiched between a heavily doped $N$-type emitter and another $N$-type collector; while in a PNP transistor, a thin and lightly doped $N$-type base is sandwiched between a heavily doped
*P*-type *emitter* and another *P*-type *collector*. The BJT is composed of two junctions. Indeed, in order to fabricate this type of transistor, a deep knowledge about diodes is necessary.

![BJT schematics and structures. (a) NPN transistor, (b) PNP transistor. The three terminals of the BJT are called the Base (B), the Collector (C) and the Emitter (E).](image)

**1.8.2 Working principle**

In a word, the voltage between two terminals controls the current through the third terminal, which is the basic principle of a transistor. In the following we will take NPN BJT as an example. With the voltage $V_{BE}$ (voltage between the base and emitter) and $V_{CB}$ (voltage between the collector and base) as shown in the figure 1.18, the Base-Emitter (B-E) junction is forward biased and the Base-Collector (B-C) junction is reverse biased. The behavior of the NPN transistor is determined by its two *P*-*N* junctions:

- The forward biased base-emitter (BE) *P*-*N* junction allows the free electrons in emitter to go through the *P*-*N* junction to arrive at the base, forming the emitter current $I_E$. 


• As the P-type base is thin and lightly doped, only a small number of the electrons from the emitter recombine with the holes in base to form the base current $I_B$.

• Most of the electrons coming from the emitter become minority carriers in the P-type base, and they go through the reverse biased collector base P-N junction to arrive at the collector.

• The percentage of those electrons that arrive at the collector out of the electrons from the emitter is defined as $\alpha$ (i.e., $\alpha = 99\% = 0.99$, depending on the doping and geometry of the material). The total collector current $I_C$ is therefore $I_C = \alpha I_E$.

The current gain or current transfer ratio is defined as the ratio between the emitter (input) current $I_E$ and the collector (output) current $I_C$

$$\frac{I_C}{I_E} \approx \alpha < 1$$, i.e. $I_C = \alpha I_E$

The base current is

$$I_B = I_E - I_C \approx I_E - \alpha I_E = (1 - \alpha) I_E$$, i.e. $I_E = \frac{1}{1 - \alpha} I_B$

The input current $I_E$ is a function of related to the $V_{CE}$ as well as the input voltage $V_{BE}$, which is much dominant

$$I_E = f(V_{BE}, V_{CB}) \approx f(V_{BE}) = \frac{1}{1 - \alpha} I_B = \frac{1}{1 - \alpha} I_0 (e^{V_{BE}/V_T} - 1)$$

Where

$$I_B = I_0 (e^{V_{BE}/V_T} - 1)$$

Similarly, The output current $I_C$ is a function of related to the output voltage $V_{CE}$ as well as the input current $I_E$, which is much dominant
Figure 1. Biasing voltages of NPN transistor and the direction of the currents and the voltage polarities.

Transistor operation and characteristic I-V curves

The three terminals of the transistors and the two junctions, present us with multiple operating regimes. Actually, we can distinguish four regimes of operation by varying the bias conditions. The output characteristic of the BJT is the plot of the collector current, \( I_C \), versus the collector-emitter voltage, \( V_{CE} \), for various values of the base current, \( I_B \), and each base current corresponds to a given \( V_{BE} \) value.

For \( V_{BC} > 0, V_{BE} > 0 \), the collector base diode is forward biased and the transistor is said to be in saturation. In this case, the collector current is the difference of the electron current injected form the emitter into the base and the electron current injected form the collector into the base. As a result, the collector current increases as \( V_{CE} \) increases, i.e., the transistor is said to be in saturation, but becomes less saturated.

For \( V_{BC} > 0, V_{BE} < 0 \), the collector base diode is reverse biased and the transistor is said to be in its normal forward active mode of operation. All the electrons injected form the emitter into the base are collected by the collector, as

\[
I_C = f(V_{BE}, V_{CB}) \approx f(V_{BE}) = \alpha I_E
\]
recombination in the intrinsic base is negligible in modern transistors, and there’s no electron injection from the collector into the base. The collector current is therefore independent of $V_{CE}$. The current gain is also constant, and the constant $I_b$ curves are spaced part by the amount determined by the base current step, as illustrated in figure 1.18.

While biasing conditions opposite of saturation (both junctions reverse biased) are present, there is very little current, which corresponds to a logical “off”, or an open switch, the transistor is said to be in the cut-off region. For the collector current $I_C$ to exceed certain critical value, resulting in damage to the transistor.

![Figure 1.19](image)

Figure 1. 19 Common emitter BJT circuit for determining output characteristics (left), and its qualitative characteristic curve (right). The plot indicates the four regions of operation: the saturation, the cut-off, the active and the breakdown. Each family of curves is drawn for a different base current and in this plot $I_{b4} > I_{b3} > I_{b2} > I_{b1}$. 


Chapter 2

Materials, Instruments and Methods

In this chapter, the main materials and instruments used during the device fabrication, and characterizations are described. Moreover, the devices fabrication procedures and measurement setup are addressed.

2.1 Materials

In this part, we will give a brief introduction to the materials selected for our devices and their specific properties that is applicable for fabrication processes.

2.1.1 N-type semiconductor

The N-type semiconductor selected for this work is Polyera ActivInk\textsuperscript{TM} N2200, or poly(N,N-bis-2-octyldodecyl-naphtalene-1,4,5,8-bisdicarboximide-2,6-diyl-alt-5,5-2,2\textsuperscript{-}bithiophene), is also known as P(NDI2OD-T2) and its number-average molecular weight of 33 kg/mol.

As a semiconducting polymer, N2200 has a high electron mobility of up to $\sim0.85$ cm$^2$/Vs under ambient conditions in combination with Au contacts and various polymeric dielectrics.\textsuperscript{[33]} It is one of the few acceptor or electron conducting polymers with good performance in ambient conditions.\textsuperscript{[34]} Its chemical structure and some experimental data of N2200 is shown in Figure 2.1 and Table 2.2,
respectively.

The polymer backbone consists of the co-monomer NDIR, N,N’-dialkynaphthalene dicarboximide, and two connected thiophene groups. The NDIR co-monomer has a high electron affinity and ensures an electron depleted electronic structure of the polymer.

![Chemical structure](image)

*Figure 2.1 P(NDI2OD-T2) (Polyera ActivInk N2200) chemical structure and energy band gap [33].*

### 2.1.2 P-type semiconductor

P-type semiconductors were discovered and improved earlier, compared to N-type semiconductor. Typically, a common character of these materials is the thiophene unit, an electron-rich group, usually used as π-conjugated unit within chain backbone, while alkali groups are bounded as substituent to improve its solubility.

As for the P-type semiconductor, in this thesis, thermo-cleavable tBoc functionalized T3DPP small molecule is selected for highly insoluble semiconducting layers in solution-processed junction diodes, which is the preliminary condition to fabricate a vertical architecture junction diode. This is a promising strategy, so-called latent
pigment methodology, first reported by Zambounis et al., where insoluble pigments are made soluble by functionalization with volatile solubilizing moieties which can then be cleaved through either a thermal or optical process, unlocking molecular interactions, such as hydrogen bonding and π-π interactions. Protective groups, like the t-butoxycarbonyl radical (tBoc), are meant to make the derivative soluble by hindering hydrogen bonds.\[39\]

This P-type molecule based on a terthiophene DPP molecule with tBoc groups on the lactam N,N positions (T3DPP-tBoc, Figure 2.2), has previously shown good potential for organic solar cells and transistors,\[35-37\] but was not investigated for junction diode applications.

![T3DPP-tBoc chemical structure and energy band gap](image)

Figure 2.2 T3DPP-tBoc chemical structure and energy band gap\[38\].

In this case, the thin film morphology of T3DPP-tBoc undergoes a strong rearrangement upon thermal deprotection of the tBoc groups, accompanied by a sharp increase of field-effect currents, leading to hole mobility up to $10^{-2} \text{ cm}^2/\text{Vs}$, and formation of H-bonding aggregates (figure 2.3), which has been verified by other researcher in our group.
During this work, the solution used for the diode fabrication was prepared by dissolving in chloroform with a concentration of 5 mg/ml. The solution has to be stored in refrigerator in order to avoid the deprotection of tBoc groups. In order to avoid effects due to degradation, a fresh solution was prepared just before fabrication.

2.1.3 Dopants

Due to the quite different structure of inorganic and organic semiconductors, one could expect significant differences of the doped semiconductors in the properties, such as electronic, morphology, et al. However, there are many similarities both in the doping fundamentals and process. The main differences in the doping behavior are due to the fact that the transport in organic semiconductor is taking place by
hopping in a distribution of more or less localized states, as stated in 1st chapter.

The elementary principle of doping is just like in inorganic semiconductors and illustrated in Figure 2.4. Electron donors or acceptors are added to the host material, providing additional mobile charge carriers. To obtain $N$-type doping in organic semiconductor, the dopants have to donate electrons to the LUMO level and therefore must have a low ionization potential. On the contrary, $P$-type dopants, having high electron affinity, extract electrons from the HOMO level, therefore, leaving holes. Furthermore, it is well known that when the charge carriers concentration is increased, the Fermi level moves toward the transport level of the organic semiconductor. In the case of $P$-type doping, the Fermi level moves toward HOMO state, while it moves to LUMO state in $N$-type doping.

![Figure 2.4 Scheme of the doping process for molecular $P$-type (left) and $n$-type doping (right). In $P$-type doping, the dopant is an acceptor, in $n$-type it is a donor.]

During this thesis work, neutral small molecule F4TCNQ and N-DPBI are selected as $P$-type dopant and $N$-type dopant, respectively.

F4TCNQ is a most common molecular $P$-type dopant, which has been widely accepted as a state-of-the-art $P$-type dopant in organic optoelectronic devices.$^{[40-43]}$

It is a strong electron acceptor, with a strong solid-state electron affinity of 5.2 eV, and its planarity enables sufficient blending with the host materials.$^{[44, 45]}$ However, an additional challenge of using F4TCNQ is the stability and processing of doped
organic films, which has to be considered for the devices with desired lifetimes of years. Recent work has shown that F4TCNQ can diffuse in small molecule and polymer semiconductor films below 80 °C while it is highly volatile as the temperature increases,[46-50] which is described in the later sections of this thesis work.

![Chemical structures of the P-type dopant F4TCNQ and N-type dopant N-DPBI.](image)

N-DPBI is a novel derivative of N-DMBI (NMe₂ versus NPh₂). As a consequence of this structure modification, the electron-donating strength of the amine functionality is decreased by replacing methyl groups with phenyl rings. Additionally, the aromatic phenyl rings stabilize the radical species through resonance, ensuring a stable doped formulation over time. Furthermore, the presence of a bulky triphenyl functionality in the N-DPBI structure changes solubility/miscibility, influencing the distribution of the dopant in the host material blend when compared with the parent N-DMBI.[51]

### 2.2 Instruments

Various instruments have been used during the thesis work. The electrodes were deposited by the thermal evaporator. The microscopic features of the thin films were observed through the use of a UV-Vis spectrometer, Atomic Force Microscope
(AFM) and X-Ray Diffraction (XRD). Electrical measurements of diode devices behaviour were measured using a semiconductor parameter analyser (SPA) in inert nitrogen atmosphere.

2.2.1 Thermal evaporator

During this thesis work, so-called Physical Vapor Deposition (PVD), or thermal evaporation was used to deposit the gold and aluminium electrodes with different thickness for the diodes.

The thermal evaporation process, is a vacuum technology for applying coatings of pure materials onto various surfaces. The thickness of the evaporated films can be easily controlled and the minimum evaporation rate 0.1 Å/s. The materials to be applied with thermal evaporation techniques can be pure atomic elements including both metals and non-metals, or can be molecules such as oxides and nitrides.

There are two primary means of heating the source material. One method, often referred to as Filament Evaporation, is a simple electrical resistive heat element, or filament, which is used in this thesis work. There are numerous different physical configurations of these filaments, including many known as “boats”-essentially thin sheet metal pieces of suitable high temperature metals (in this work, tungsten and Tantalum were selected for gold and aluminium, respectively) with formed indentations or troughs into which the material is placed. The filament source offers the safety of low voltage, although very high current is required, usually several hundred amps.
Figure 2.6 Cross sectional view of an thermal deposition system and an thermal evaporator in N2 atmosphere glove-box.

### 2.2.2 UV-Vis spectrometer

An UV-Vis spectrometer, was used to closely observe the optical features of the thin films. A diagram of the components of a typical spectrometer are shown in the following diagram in figure 2.7. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a reference glass which is covered by the film being studied. The other beam, the reference (colored blue), passes through an identical cuvette containing only the glass. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $I_0$. The intensity of the sample beam is defined as $I$. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region
scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

2.2.3 Atomic force microscope

In an atomic force microscope (AFM), a sharp tip is mounted at the end of a cantilever. The general set up is shown in Figure 2.8. The vertical displacement of the cantilever, and thereby the force between the tip and the sample, is measured and plotted against the position of the tip in the sample plane. The vertical displacement of the tip is commonly measured by a laser that is reflected at the back of the cantilever.

The deflection of the cantilever is influenced by all forces between the tip and the
sample. This includes mainly Van der Waals forces and contact forces. During this thesis work, AFM was used to investigate the surface morphology of the doped thin film.

2.2.4 X-Ray Diffraction

A X-ray Powder Diffraction (XRD), Bruker D8, was used to observe the difference in crystal structures before and after annealing processes of the semiconductors. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample.

![Diagram of the components of a typical XRD and its working principle.](image)

The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a
range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.

2.2.5 Oscilloscope

An oscilloscope (Tektronix MSO 4054 Mixed signal Oscilloscope was used in this thesis work) is a laboratory instrument commonly used to display and analyze the waveform of electronic signals. In effect, the device draws a graph of the instantaneous signal voltage as a function of time. The basic oscilloscope, as shown in the illustration, is typically divided into four sections: the display, vertical controls, horizontal controls and trigger controls. The display is usually a CRT (cathode ray tube) or LCD (liquid crystal display) panel which is laid out with both horizontal and vertical reference lines referred to as the graticule. In addition to the screen, most display sections are equipped with three basic controls: a focus knob, an intensity knob and a beam finder button.

The vertical section controls the amplitude of the displayed signal. This section carries a Volts-per-Division (Volts/Div) selector knob, an AC/DC/Ground selector switch and the vertical (primary) input for the instrument. Additionally, this section is typically equipped with the vertical beam position knob.

The horizontal section controls the time base or “sweep” of the instrument. The primary control is the Seconds-per-Division (Sec/Div) selector switch. Also included is a horizontal input for plotting dual X-Y axis signals. The horizontal beam position knob is generally located in this section.

The trigger section controls the start event of the sweep. The trigger can be set to
automatically restart after each sweep or it can be configured to respond to an internal or external event. The principal controls of this section will be the source and coupling selector switches.

Figure 2.10 Schematic representation of the components of a typical oscilloscope.

2.2.6 Semiconductor parameter analyser

A glove-box under inert atmosphere, featuring a maximum allowed amount of water and oxygen of 0.1-0.5 ppm, was used to store the fabricated devices. The sample to be analyzed is put on an holding plate, and an optical microscope connected to a CCD camera provides a top-view of the sample at a high magnification. The holding plate is equipped with four electrical probes, connected to the outside of the glove-box via coaxial cables. Each probe allows careful positioning of its tip over the
desired point of contact with the aid of three micromanipulators, one for each axis. The probes are connected to the Agilent B1500A Semiconductor Device Analyzer measurement system that, among the other, can perform I-V measurements, with a resolution of 0.1 \( fA \) and 0.5 \( \mu V \).

In our experiments, the performances of junction diodes were analyzed performing static and AC measurements. Two tips were connected to the device and applied voltages were defined via software.

![Figure 2. 11 Photo of the semiconductor parameter analyzer (left) and the prober in glovebox (right)](image)

### 2.3 Methods

In this section, the fabrication procedures for the junction diodes realized during this thesis work, as well as the doping method for both P- and N-type semiconductors used during the experiments are described.

#### 2.3.1 Doping process

Here two different doping methods for both P- and N-type semiconductors are performed: mixed solution doping method and sequential doping method, and the conductivity of the doped semiconductors were studied.
Mixed solution doping method for T3DPP

Before use, T3DPP was dissolved in chloroform (CF). F4TCNQ powder was dissolved also in CF and keep at 50 °C overnight to get a homogeneous solution. Immediately before spin coating, T3DPP solutions were mixed with F4TCNQ at 50 °C to give solutions with various concentrations. The concentrations of T3DPP and spin coating speeds were varied to obtain different thick films.

Sequential doping method for T3DPP

Thin films of T3DPP were prepared by spin coating T3DPP (5 mg/ml in CF) at 500-1000 rpm for 1 min to form 50-100 nm thick films. The samples were annealed at 200 °C for 5 mins. Doping was performed by wetting the film with F4TCNQ (various concentrations, 0.05, 0.3, 0.1 mg/ml in CF), waiting 6 seconds, then spinning off the excess solution at 1000 rpm for 30 s.

Mixed solution doping method for N2200

Figure 2. 12 Schematic of the two doping methods for T3DPP.
Before use, N2200 was dissolved in dichlorobenzene (DCB) and kept at 60 °C overnight to get a homogeneous solution. N-DPBI powder was dissolved also in DCB and it dissolved immediately. Immediately before spin coating, N2200 solutions were mixed with N-DPBI to give solutions with various doping concentrations. The concentrations of N2200 and spin coating speeds were varied to obtain different thick films.

2.3.2 Device fabrication

Junction diodes

P-N junction diodes fabricated based on inorganic or inorganic-organic hybrid diodes, show good performances, i.e., high current density (1 A/cm²), high rectification ratio, low turn-on voltage. In this thesis, however, all the diodes are fully organic.

In this thesis, the vertical architecture is preferred due to its relatively easy fabrication processes. The junction diodes fabricated on the glass (2 cm²), a standard microscope slide was cleaned through the following three steps of sonication (ten minutes each) in a millipore water, acetone, iso-propanol immersion. Then O₂ plasma cleaning was applied for five minutes. In order to obtain a good adhesion, 2.5 nm Chromium (Cr) was deposited on the samples before the 30 nm Au deposition, which was done by the thermal evaporation on high vacuum environment.

After that, the different concentrations of T3DPP-tBoc/(F₄TCNQ) were spin-coated on the glass substrates and annealed at 200 °C for 5 mins in air, to obtain the thin films with different thickness. While in the case of N2200/(N-DPBI), it was deposited by spin-coating on the samples at 1000 rpm for 30 s. Solvent was evaporated by
heating the sample at 105 °C for 15 minutes. The processes of deposition and annealing were performed in the N₂ atmosphere glove-box.

Then, 70 nm Aluminium was deposited on top of the N2200 layer by the thermal evaporation on high vacuum environment.

![Figure 2. 13 Schematic diagram of the structure of Au/T3DPP/N2200/Al diodes.](image)

### 2.3.3 Conductivity extraction

In this case, the organic semiconductor samples were deposited on glass (1 cm²), a standard microscope slide was cleaned through the following three steps of soni-cation (ten minutes each) in a millipore water, acetone, iso-propanol immersion. Then O₂ plasma cleaning was applied for five minutes. In order to obtain a good adhesion, 2.5 nm Chromium (Cr) was deposited on the samples before the 30 nm Au deposition, which was done by the thermal evaporation on high vacuum environment.

After that, the T3DPP-tBoc with different contents of F₄TCNQ were spin-coated on the glass substrates and annealed in air, while in the case of N-DPBI/N2200, the processes of deposition and annealing were performed in the N₂ atmosphere glove-box. The measurements were performed by two tips prober in N₂ atmosphere glove-box.
The conductivity was extracted based on the measurement of resistance by

\[ R = \rho \frac{L}{A} = \frac{\Delta V}{\Delta I} \]

Where the \( \rho \) is electrical resistivity, \( R \) is the electrical resistance, \( L \) is the length of the piece of material, and \( A \) is the cross-sectional area of the specimen. Its SI unit is “Ohm metre” (\( \Omega \cdot m \)). Then since the conductance, \( G \)

\[ G = \frac{1}{R} = \sigma \frac{A}{L} \]

Where the \( \sigma \) is the conductivity, therefore the

\[ \sigma = G \frac{L}{A} = \left( \frac{\Delta V}{\Delta I} \right)^{-1} \times \frac{L}{A} \]

And it has SI units of “siemens per metre” (\( S/m \)).
Figure 2. 15 I-V curve for extraction of the conductivity, eg. T3DPP sequential doped from 1mg/ml solution for 6s.

2.3.4 DC measurements

For the DC measurements, the characteristic of the diodes were obtained by measuring the current versus voltage variation. Parameters such as rectification ratio and turn-on voltage and the ideality factor can be extracted from these curves. Typically, the anode voltage is swept from -1V to 1V, with 50 mV step, while the cathode voltage is kept constant to 0 V. In the meantime, the current flowing through the device is measured.
2.3.5 AC measurements

For the AC measurements, to analyze the frequency behaviour of the diodes, the following setup is used. The input sinusoidal waveform, with an amplitude of +1Vpp,
is provided by a waveform generator (Keithley 3390 50 MHz) and it was fed to the anode of the diode. The current at the cathode is collected by a transimpedance amplifier, which has a gain of $2 \times 10^3$, the voltage output of which was then provided to the oscilloscope, which allows to visualize the output signal.
Chapter 3

Conductivity of doped films

In this chapter, we report the conductivity properties and the film morphology of N2200 and T3DPP, which were obtained by application of N-DPBI and F4TCNQ, respectively. Furthermore, in order to explain the results we got, we also propose doping mechanism and models.

3.1 N2200 doped with N-DPBI

In order to study the electric properties of N2200 extrinsically doped with N-DPBI, we spin coated one 50 nm thick films from DCB solution with the undoped N200, while four N2200/N-DPBI mixture solutions with different weight ratio concentrations of 8 wt%, 10 wt%, 15 wt% and 20 wt% were prepared just before use. Conductivity was then measured in a two-probe geometry, using pre-patterned Au contacts on top of glass substrates and extracting $dI/dV$ for multiple devices per sample, as stated in chapter 2.

The average conductivities for each sample are shown in figure 3.1. The pristine N2200 exhibits a poor conductivity of about $1.3 \times 10^{-8}$ S/cm. However, as expected for successful extrinsic doping, a dramatic increase in the conductivity of the film is observed. Precisely, increased with progressively larger amounts of the molecular dopant N-DPBI, the conductivity of N2200 rapidly increases by 5 orders of magnitude.
to about $10^{-3}$ S/cm.

![Graph showing conductivity vs. doping concentration.]

*Figure 3.1 Conductivity and measurement of pristine and N-DPBI doped N2200 films at different doping concentrations.*

The nature of the doping of N-DPBI has been studied for fullerene derivatives and even similar molecules like N2200,$^{[52-54]}$ and hereby we outline the possible mechanisms, see figure 3.2. For N2200, we rule out a simple charge-transfer mechanism for doping, as the HOMO of N-DPBI lies at a lower energy (-4.6 eV) than the LUMO of N2200 (-4.0 eV).

![Diagram showing reaction mechanism.]

*Figure 3.2 Possible reaction mechanism for the N-doping reaction of N2200 with N-DPBI.*

To determine why so few dopants actively donate electrons to the conduction states of N2200, the morphology of the films was characterized by AFM. As found also in
the literature, the electronic conductivity saturation observed in Figure 3.1 for N2200 at N-DPBI doping concentration 15 wt% is probably due to inefficiencies of the dopant rather than an intrinsic limitation of the polymer.\cite{55} The AFM images of undoped film shows fiber-like structure as previously reported.\cite{33} While the doped films reveal the formation of aggregates on the top surface that are not present on the surface of pristine N2200 films. In other words, the pristine film shows fiber-like structure, while the N-DPBI doped film at 15 wt% shows grainy aggregates, which indicates significant phase segregation of the molecular dopant. This observation is also in agreement with previous studies showing similar phase segregation of molecular dopants in the polymer host films for N-DPBI dopant ratio >10 mol %.\cite{52}

![AFM images](image)

*Figure 3. 3 AFM height images of (left) pristine N2200 thin film and (right) N2200 thin film doped with 15wt% of N-DPBI. The rms roughness for two films is 1.08 and 1.55 nm, respectively.*

### 3.2 T3DPP doped with F4TCNQ

As shown in figure 3.4, upon the thermal treatment at 200 °C, the absorption bands are strongly blue shifted with respect to the non-deprotected films, with the appearance of a sharp feature at 563 nm that can be attributed to a densification effect after the removal of the tBoc groups. Correspondly, The AFM topography of
the T3DPP-tBoc film before deprotection (Figure 3.5b, c) is characterized by rod-like beads, the dimension of which appear smaller after deprotection.

![Graph showing UV-Vis characterization of T3DPP-tBoc and T3DPP after deprotection.](image)

*Figure 3.4 UV-Vis characterization of T3DPP-tBoc and T3DPP after deprotection.*

The corresponding XRD patterns (Figure 3.5a), measured on the same film, show a diffraction peak at \(2\theta = 7.7^\circ\) before deprotection, indicating the presence of a crystalline phase. Such peak completely disappears with cleavage, after which only a small and broad signal at low angle values is present, which is rightly perfected according to Bragg’s law. Furthermore, there is a significant decrease in film thickness from 40 to 29 nm and an increase in surface roughness from 1.3 to 3 nm, indication of significant changes within the film after cleavage and the tBoc loss, accompanied by coloration from blue to purple.
Figure 3.5 XRD and AFM topography images for T3DPP-tBoc and T3DPP after deprotection.

In the case of T3DPP doped with F4TCNQ, Figure 3.6 and 3.7 shows AFM images of T3DPP films doped using the mixed solution process (3.6) and the sequential process (3.7). As is clearly visible in Figure 3.6, the mixed solution method yields significantly rougher films due to the dopant F4TCNQ tend to aggregate in the film. Furthermore, considering the RMS (root mean square) roughness calculated from these images, even doping at 5 wt% results in some doubling of RMS roughness compared to as-coated films, increasing to 3.1 nm from 1.4 nm.

In contrast, the sequentially doped T3DPP films in Figure 3.6 show morphology essentially identical to as-cast up to 1 mg/ml. Actually, no significant phase segregation is visible. The samples further shows nearly the same phase segregation level even though doped from higher concentration solution (1 mg/ml). As shown in the UV-Vis spectrum, as the F4TCNQ weight ratio is increased, absorption bands corresponding to the F4TCNQ radical anion (350-400 nm) grow in. These observations suggest that sequential doping allows a significant fraction of F4TCNQ to infiltrate T3DPP crystallites.
Figure 3. Tapping mode AFM height images of F4TCNQ doped T3DPP films using the mixed solution method. Doping level of F4TCNQ in wt% is indicated above each image for mixed solution films. All images are 5 µm square and plotted with the same height scale (15 nm).
Figure 3. 7 Tapping mode AFM height images of F4TCNQ doped T3DPP films using the sequential doping method. Doping level of F4TCNQ in mg/ml is indicated above each image for mixed solution films. All images are 5 μm square and plotted with the same height scale (15 nm), and the corresponding UV-Vis spectra.
Figure 3. 8 (a) Conductivity of T3DPP films exposed to a 1 mg/ml solution of F4TCNQ dissolved in Chloroform for times between 1 and 60 seconds (time indicate the duration of dopant solutions on top of the T3DPP layer before spinning off), while the 0 s indicate the pristine film. (b) sequentially coated T3DPP/F4TCNQ films, where the dopant has been first deposited and then spin off after waiting for 6 seconds and (c) conductivity data of mixed solution films.

The doping-induced formation of aggregates in solution has negative effects on the electrical properties of the resulting films. This issues are nicely avoided by sequential doping, as shown in figure 3.7. Figure 3.8a shows the conductivity of the T3DPP films doped from F4TCNQ dissolved in Chloroform with a concentration of 1 mg/ml by sequential doping method for times between 1 and 60 s. The extremely weak dependence on exposure time to dopant solution suggests the establishment of an equilibrium between the neutral F4TCNQ in the solvent and ionized F4TCNQ in the T3DPP matrix. This equilibrium is clearly reached in more or less 6 seconds,
resulting in a relatively high conductivity in the order of magnitude of 0.1 S/cm. As expected, in the case of sequential doping method, see figure 3.8b, increased doping solution concentration increases the film doping level, leading to conductivities controllable over more than 6 orders of magnitude, reaching a high conductivity of 0.1 S/cm for the sample doped with the dopant solution of 1 mg/ml. In the case of the mixed solution doping method, instead, the conductivity is slightly increased by 2-3 orders of magnitude with respect to the undoped film. On one hand, one could attribute this to the formation of the aggregates in the resulting films as we stated before. Also, another main reason is due to the F4TCNQ is quite volatile when the temperature is higher than 80 °C.\textsuperscript{[46-50]} Actually, since the mixed solution method doped T3DPP has to be annealed at 200 °C in order to deprotect it, most likely only few amount of F4TNCQ are left after the annealing process.

Figure 3. 9 Morphological development in mixed-solution and sequential doping. In the mixed solution process (a), initially solvated T3DPP aggregates in solution upon addition of F4TCNQ. When these aggregates are spun into a film, they form disconnected crystallites, with few tie chains (shown
in blue). As a result, in an applied electric field, polarons cannot move easily between crystallites (shown upper right). The sequential process (b) avoids this issue since film morphology is set by initial film casting conditions. Doping from CF leaves F4TCNQ counter-ions only in amorphous domains, while polarons move to crystalline domains, allowing for unimpeded flow of charge.

Based on the comparisons in the morphological differences between the mixed solution doping and sequential doping methods, we could find a probable interpretation for the conductivity data in the context of tie chains. As shown in figure 3.9a, it suggest mixed-solution films are composed of discrete, pre-formed crystallites with relatively few chains connecting them. Consequently, we see a significant reduction in the mobility of charge carriers between crystallites, and also an increase in trapped charge carriers. However, in the sequential doped films (figure 3.9b), morphology is set by the initial T3DPP spin coating, which creates a morphology with more tie chains between crystalline domains. Doping does not significantly change this morphology, allowing for higher conductivity at a given doping level, which agrees well with the observations from the AFM images before.

3.3 Conclusions

In this chapter, high conductivity of both N2200 and T3DPP semiconductor have been achieved, by using N-DPBI and F4TCNQ dopants, respectively. The highest conductivity for N2200 is $2 \times 10^{-3}$ S/cm and was obtained by mixing the N-DPBI dopant with the N2200 in a concentration of 15 wt% N-DPBI. For the case of T3DPP, it reaches 0.05 S/cm by sequentially spin coating the F4TCNQ dopant solution of 1mg/ml dissolved F4TCNQ in chloroform on top of the T3DPP film. On the other
hand, the conductivity of T3DPP doped by mixed the semiconductor and the dopant in solution, shows only a 2 orders of magnitude increase compared to the pristine film. The morphology of the doped films, were then studied by the AFM technique, showing the presence of aggregates of the F4TCNQ in the film doped with the mixed solution method, resulting in phase segregation. Based on the comparisons in the morphological differences between the mixed solution doping and sequential doping methods, we can infer that mixed solution films are composed of discrete, pre-formed crystallites with relatively few chains connecting them, leading to a less pronounced increase in conductivity. For the sequential doped films, instead, morphology is set by the initial T3DPP spin coating, which creates a morphology with more tie chains between crystalline domains. Doping does not significantly change this morphology, allowing for higher conductivity at a given doping level.
Chapter 4

P-N Junction diodes

In this chapter, we go through the performance of our undoped and doped diodes. First, the diodes with undoped semiconductors are described, and the dependence of the thickness and area of the diodes is addressed. Furthermore, diodes with doped semiconductors are realized.

4.1 Junction diodes with undoped semiconductors

We firstly fabricated the 3 diodes with two pristine semiconductors by varying the active area and thickness of T3DPP, as shown in the figure 4.1. We observed the rectifying behaviours in all the diodes. The rectifying behaviour can be explained by looking at the energy levels illustrated in Figure 4.1b. Indeed, the Au electrode, which has high work function, easily injects hole carriers into the HOMO level of the P-type T3DPP, when the diodes are in the forward bias. Whereas, when the diodes are reverse biased, hole carriers are hardly injected from Au electrode into the HOMO level of the T3DPP, because of the increased energy barrier.

As expected, the diodes with the active area of 0.25 mm$^2$ obtained better performances with respect to 1 mm$^2$, in terms of high rectification ratio about $10^3$, with a low turn-on voltage about 1V. This is likely due to the fact that stacking dissimilar materials over wide areas is inherently prone to generating defects at the
interface. This is also confirmed by the extracted ideality factors, as shown in the figure 4.1c. Indeed, the lowest ideality factor is found for the lowest area device, n=17, indicating that it was the one closest to the ideality. The current density obtained by applying reverse voltage, is pretty constant when varying the thickness of T3DPP layer, while it varies heavily when on the thickness of N2200 is varied, as shown in the figure 4.2. the reverse current density shows significantly different by only varying the thickness of the N2200 layer. This suggests that the reverse current is pretty much dependent on the thickness of the N2200 layer.

![Diagram](image)

*Figure 4. 1 (a) Schematic of the P-N junction diodes, (b) energy level diagram of the semiconductors and the electrodes and (c) J–V characteristics for each diode. Note the active area of the diode are 1mm² and 0.25 mm².*

When deeply look in to the J-V curves of the diodes, two distinct regions are
observed under forward bias, as shown in figure 4.1c: I) Ohmic region; II) Space charge limited current (SCLC) region. In region (I), where applied voltage is so small that injected carriers are unable to fill any traps in organic materials and hops between the deepest energy traps, as a result, the current is proportional to the applied voltage. As for region (II), all traps are filled, free carriers transport in organic materials but limited by the space charge supported by the excess electric charges. As stated in the first section of this thesis, Mott-Gurney’s model can well describe the space charge limited current. The lowest ideality factor that we obtained was about 17 for the 0.25 mm$^2$ active area diodes, as shown in the figure 4.1c.

![Figure 4.2: Schematic of the P-N junction diodes (inset) and the J-V characteristics for each diode.](image)

The active area is 0.25 mm$^2$ for all the diodes, the thickness of N2200 is varying while the T3DPP layer is kept constant to 50 nm.
In order to further understanding of where the rectifying comes from, we then fabricated the “sandwich” architecture diodes with only one semiconductor, as shown in the figure 4.3. Interestingly, we found that there’s no rectification behaviour observed from all the diodes no matter what’s the semiconductors used.

Figure 4.3 Schematic of the diode with different semiconductors (b) T3DPP (c) N2200, and the corresponding current density vs. voltage (J-V) characteristics.

4.2 Junction diodes with doped semiconductors

In order to obtain a diode with higher free carrier concentration, the doping of the semiconductor is introduced. Firstly, we try to only dope T3DPP layer, and the results as shown in the figure 4.4. We found that the diode with T3DPP doped by sequential doping method, shows symmetric J-V characteristic, but on current density is the same to the undoped diode. The loss of rectification could be attributed to the fact that the F4TCNQ diffuses into the N2200 layer during the following annealing process of the N2200. In the contrast, the diode shows little rectification ratio about
1-10, which could result from the difference of conductivity between the sequential and mixed solution doping method. Although this, we still could further our research to explore a stable dopant that can sustain high temperature and better understand the effects of doped layers when used in a diode configuration.

Figure 4. Schematic of the P-N junction diodes (inset) and the J–V characteristics for each diode. The active area is 0.25 mm² for all the diodes, the thickness of both N2200 and T3DPP are always 50 nm. T3DPP was doped by different doping method: sequential doping from 1 mg/ml F4TCNQ in CF and mixed solution doping from the T3DPP/15 wt% F4TCNQ in CF.

4.3 Conclusions

The performances of the junction diodes have been investigated. We successfully fabricated a diode with a high rectification ratio of $10^3$ and low turn-on voltage by using pristine semiconductor layers, Unfortunately, the diodes with doped
semiconductors, were not working, most likely due to the diffusion of F4TCNQ dopant into the N2200 layer. Further studies of the doped layers behaviour when put in a diode structure are then necessary.
Chapter 5

Rectifier application

In this chapter the frequency response of the diodes fabricated with pristine semiconductors, to AC signal input is addressed. To start, a rectifier circuit was introduced. The diodes show good rectifying behaviour up to 1 KHz AC signal input, which agrees well with the theoretical calculations.

5.1 Rectifier

The rectifier is one of the key components for organic radio-frequency identification (ORFID),\textsuperscript{[59]} which has been considered as a potential application of flexible, low cost electronic products. High on/off ratio and high-frequency operation of organic rectifier diodes have been demonstrated.\textsuperscript{[60]} There are two competing approaches for making an organic rectifier.\textsuperscript{[61]} It can be based either on an organic thin-film transistor (OTFT) with shortened drain-gate or on a vertical organic diode.\textsuperscript{[62-66]} Although easier to integrate, using an OTFT in a rectifier requires an organic semiconductor with a much higher mobility, because of the larger lateral channel length compared with the much shorter vertical layer thickness of an organic diode. However, it needs to be considered that the mobility extracted out of the space-charge-limited current regime of a diode is normally lower than the
field-effect mobility shown for OTFTs due to the higher charge density achieved in
the channel of transistors compared with diode structures.\textsuperscript{[67]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_1.png}
\caption{Rectifier circuit diagram for rectifying effect of Au/T3DPP/N200/Al junction diodes (a); Architecture of the diode used to frequency test (b). (The active area is 0.25 mm\textsuperscript{2}, $C_L=100$ nF, $R_L=1$ M\textOmega, the series resistance of 50 \textOmega indicates the internal resistance of the function generator)}
\end{figure}

5.2 Characterizations

In this thesis work, for the vertical organic diode approach, hereby we used the
undoped junction diode, as shown in the figure 5.1b. The rectifier circuit composed
of the diode in parallel with its parasitic junction capacitance, which are connected
to the virtual ground of the transimpedance amplifier. The rectifier was driven by a
sinusoidal wave form generator with a negligible 50 \textOmega series resistance.

As a first approximation, we can simply think the diode as a resistor which is in
parallel to a capacitor. If the impedance of the diode capacitor is lower than that of
the resistor, most current flows through the parasitic capacitance of the diode,
resulting in a non-rectified output voltage. We can estimate here the frequency at
which the impedance of the diode capacitor is equal to the resistor one.

The impedance of the diode junction capacitor decreases as the frequency increases
where the \( f \) is the input signal frequency and the \( C \) is the capacitance of the diode.

The resistance of the diode can be instead calculated from its static characteristic as

\[ R = \left( \frac{\partial I}{\partial V} \right)^{-1}. \]

So, the frequency at which the impedance of the diode capacitor is equal to the resistor is

\[ f = \frac{1}{2\pi RC}. \]

Since the geometry of the diode in our case is a parallel-plate, the capacitance is calculated by

\[ C = \varepsilon_r \varepsilon_0 \frac{A}{W}. \]

Where the \( A \) is the active area of the diode, \( W \) is the thickness of the depletion region, \( \varepsilon_r \) and \( \varepsilon_0 \) is the relative permittivity and the vacuum permittivity, respectively.

In this case, using the above mentioned formulas, we obtain a capacitance of \( C=1.5\text{pF} \), using a relative constant of 3.5 for both N2200 and T3DPP, and a depletion region \( W \) of 50 nm which is reasonable for organic diodes.\(^{[60]}\) The value of the resistance of the diode is instead of about 110 kΩ, and it was calculated from the \( I/V \) characteristic of the diode. Using these values, we calculate a crossing frequency of about 9.3 kHz. In the calculation we neglect the diffusion capacitance component, the contribution of which is usually dominant in forward biased inorganic diodes.
Figure 5.2 Rectifying signal of the diode under different input frequency. (Diode size: 0.25 mm², CL=100 nF, RL= 1 MΩ)

The rectifier output was monitored with both an oscilloscope. As shown in the figure 5.2, when the input AC frequency is 100 Hz, the diode has a good rectifying behaviour. This means the impedance of the parallel capacitor is higher than the diode’s resistor. However, when the input frequency is 1 KHz or even higher, the diode shows poor rectifying response, because of the influence of the parallel parasitic capacitance, in agreement with our rough estimation.

5.3 Conclusions

In this chapter, the frequency behaviour of the junction diode have been studied, showing good rectifying behaviour up to 1 kHz input AC signal. Above this frequency, the influence of the parasitic capacitance is not negligible and the diode loses its
rectification behaviour. A rough estimation of the maximum frequency of operation of the device gives a value of 9.3 kHz, the order of magnitude of which is in agreement with the experiments. As further work, it would be possible to increase the frequency of operation of the devices in a straightforward way by reducing the area.
Conclusions

Synopsis of results

In this thesis work, at first, we have fabricated and characterized $P$-$N$ junction diodes with fully solution processing T3DPP and N2200 as $P$- and $N$-type semiconductor, respectively. The diodes were fabricated in a vertical architecture on glass substrates, and the Au and Al electrodes were deposited by thermal evaporation. The undoped devices demonstrated good diode characteristic behaviour, with high rectification ratio of $10^3$ and low turn-on voltage of 1 V.

Then study of the effect of suitable dopants, the N-DPBI and F4TCNQ for the $N$-type and $P$-type semiconductors, was carried on. Two different doping methods were used, the mixed solution doping method and sequential doping method. The highest conductivity for N2200 is $2 \times 10^{-3}$ S/cm and was obtained by mixing the N-DPBI dopant with the N2200 in a concentration of 15 wt%. For the case of T3DPP, it reaches 0.05 S/cm by sequentially spin coating the F4TCNQ dopant solution of 1mg/ml dissolved in chloroform on top of the T3DPP film. On the other hand, the conductivity of T3DPP doped mixing the semiconductor and the dopant in solution shows only a 2 orders of magnitude increase compared to the pristine film. Unfortunately, the diodes fabricated with the doped layers did not work, suggesting that further work is necessary to better clarify the effect of the dopants in the diode.

Finally, the frequency response of the $P$-$N$ junction diodes was measured and the rectification of a sinusoidal signal was also successfully demonstrated. A probable
theoretical calculation was also applied to explain that the maximum frequency operation of this \( P-N \) junction diode.

**Future work**

It has been shown in the literature that the use of the dopant with high thermal stability could further increase the conductivity and eliminate some probable defects that formed in the interface of the junction. Therefore, we expect that we could synthesize new molecular dopant or continue to screen the suitable dopant, which could stand such a high annealing temperature. Also, we could apply the thermal evaporation method for the doping of the semiconductors or even could change the \( N \)-type semiconductor, which has been verified from our collaborative group. Experiments meant to conform this idea are on schedule. Dating back to our original idea, which is to fabricate a bipolar junction transistor, we could move this work forward. This means that we could have a try to fabricate a transistor with this kind of architecture of Au/PN junction/Al/PN junction/Al.
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