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Final Thesis

To get the degree
Of Master in Sciences of Industrial Engineer
Section: **Industry**

Training Unit of reference: **Energy Unit**

Fabrication and characterization of thin-film transistors with organic heterostructure of pentacene and PTCDI-C_{13}

Gramme Mentor
Didier MARECHAL
Assistant lecturer

Entreprise Mentor
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Associate professor

Thesis presented by

Jérôme TILMAN

Public defense
28 June 2010

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Abstract

Title: Fabrication and characterization of thin-film transistors with organic heterostructure of pentacene and PTCDI-C_{13}

This final thesis aims to advance research on the use of organic materials to produce devices such as OTFTs (Organic Thin-Film Transistors) or solar cells. Therefore, several OTFTs were performed to investigate the behavior of two organic semiconductors: pentacene and N,N′-ditridecyl-3,4,9,10-perylenetetracarboxylic diimide (commonly called PTCDI-C_{13}). They were used alone or together to form some OTFT samples (simple and with heterostructure). Good electrical characteristics were found by measuring. Regarding multilayer OTFTs, ambipolar behavior were found, what is very interesting. The innovation of this project lies in the fact that all the manufacturing steps were performed at low temperature, including the dielectric (around 150°C) composed of Al_2O_3. It should be noted that ambipolar devices have never been carried out at less temperature. Finally, the samples were submitted to the lighting of different LEDs, chosen according to the wavelengths absorbed by each semiconductor. The principal aim of this final thesis part is to see if it can be interesting to use these materials in solar cells and should be seen as an introduction for further study.

Keywords: OTFT – ambipolar TFT - Pentacene – PTCDI-C_{13} – Organic solar cells

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Titre: Fabrication et caractérisation de transistors à couches fines (TFT) avec heterostructure organique de composée de pentacène et de PTCDI-C_{13}

Ce mémoire a pour but de faire avancer la recherche sur l’utilisation de matériaux organique dans des composants comme les OTFTs (Organic Thin-Film Transistors) ou les cellules photovoltaïques. Dans ce but, plusieurs OTFTs ont été réalisés to étudier le comportement de deux semiconducteurs organiques : le pentacène et le *N,N′*-ditridecyl-3,4,9,10-perylenetetracarboxylic diimide (communément appelé PTCDI-C_{13}). Ils ont été utilisés seuls ou ensemble pour constituer des échantillons de OTFTs (simples et avec hétérostructure). Les caractéristiques d’output, de transfert et de saturation ont été établies pour chaque échantillon. Ceux-ci montrent de bonnes caractéristiques électriques. En ce qui concerne les OTFTs à multicouches, un comportement ambipolaire a été observé, ce qui est très intéressant. L’innovation de ce projet réside dans le fait que toutes les étapes de fabrication des échantillons ont été réalisés à basse température, incluant le diélectrique (à 150°C) composé de Al_2O_3. Il est à noter qu’à cette date aucun transistor ambipolaire n’a jamais été réalisé à si basse température. Finalement, les échantillons ont été soumis à l’éclairage de différentes LEDs, choisies selon la longueur d’onde absorbée par chaque semiconducteur. Le principal but de cette partie du mémoire est de voir s’il peut être intéressant d’utiliser ces matériaux dans les cellules photovoltaïques et doit être vu comme une introduction à une étude plus approfondie.

Mots clés : OTFT – TFT ambipolaire - Pentacène – PTCDI-C_{13} – cellule photovoltaïque organique

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After about 4 months of work on this thesis I would like to thank all the people without the help of which my final thesis would have not been possible.

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I also thank Miss Stephanie Cheylan and Mister Miguel Garcia for helping me in the samples realizations. I especially rend thanks to Mister Albert Marsal for all the time during which he taught to me how to make and how to measure OTFTs.

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Finally, I would like to thank everybody who was important to the successful realization of this thesis, as well as expressing my apology that I could not mention personally one by one.

Preface

In this final thesis, the TFT heterostructure[1] (specifically the field-effect structure) is employed to study the semiconductors behavior. The study is focused on different types of semiconductor materials: P-type with pentacene, N-type with *N*,*N′*-ditridecyl-3,4,9,10-perylenetetracarboxylic diimide (commonly called PTCDI-C_{13}) and these two latter to form two different heterostructures (see Chapter 9.1).

The innovation of this project lies in the fact that all the manufacturing steps were performed at low temperature, including the dielectric (around 150°C), composed of Al_2O_3. The results are sanguine because the two samples with heterostructure are ambipolar, what has never been carried out at so less temperature. Indeed, organic ambipolar TFTs exist but using usually SiO_2 as dielectric, what is realized around 1000 °C. In order to better understand, some comparisons are made with inorganic TFTs and MOSFETs, which have some similar behaviors.

The electrical characteristics (output, transfer and saturation) were found for each sample. The analysis results of the simple OTFTs are encouraging because of their good electrical characteristics. Regarding multilayer OTFTs, ambipolar behaviors were found, what is very interesting because offers inter alia the possibility to fabricate CMOS inverter[2] using the same transistors. All these results are very similar to what exists in the literature, which is very interesting since all the samples were performed at low temperature.

Lastly, the samples were submitted to the lighting of different LEDs, chosen according to the wavelengths absorbed by the two semiconductor layers. Some interpretations are made by analyzing the output, transfer and saturation graphs, with the principal aim to see if it can be interesting to use it in solar cells. The results of the two simple OTFTs are easy to analyze because the influence of the wavelength absorbed by the semiconductor is clearly visible. The interpretation is not so easy concerning ambipolar OTFTs. Since we are only at the first steps of research of this

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[1] Thin Film Transistor with a bilayer structure of two different semiconductors

[2] CMOS (Complementary metal-oxide-semiconductor) requires usually a P-type and a N-type transistors

sort of devices with illumination, it is relatively more difficult to thoroughly analyze the results. The chapter 10, concerning illumination, should be seen as an introduction to further study of this sort of sample. It should be noted that another student takes over this study.

This innovative study opens possibilities for development and improvement. Better electrical characteristics can be researched by adjusting the manufacturing specifications as the deposition rate of each layer, the substrate temperature and the layers thicknesses.

Table of contents

1 Introduction

Organic semiconductors have gained prominence these last decades. There are very important by their diversity. Indeed, materials can be made from the menu by chemical processes relatively simple and cheap. Moreover, they can be deposited on large areas at low temperature (below 200 °C), what allows the manufacture of devices on flexible substrates (as plastics).

Basically, there are three classes of organic devices: OLEDs (Organic Light Emitting Diodes), solar cells and OTFTS (Organic Thin Films Transistors). Regarding OLEDs, a voltage is applied and they emit light. In solar cells it is the opposite, they are illuminated and produce an electrical voltage. Finally, the OTFTs are commonly used as switches.

OLED technology is already very advanced. The first white light OLEDs are already marketed and will replace the compact fluorescent lamp in the coming years. Indeed, the light emitted has a higher quality and is more intense, lifetime is much longer, and the power consumption is much lower [19]. Moreover, they offer the possibility to create thin flexible panels. The operating principle of this device is to apply tension on their electrodes to emit light (See Figure 1.1).

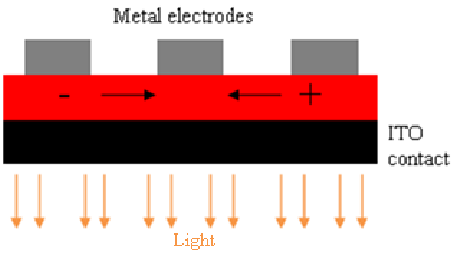

Figure 1.1. Basic operation of OLEDs

Regarding solar cells, research is less developed. Currently, with organic semiconductors, the higher conversion efficiency of sunlight into electrical voltage is 7.7%, but only in laboratory (against more than 24% with inorganic materials). The device is able to create a current between two electrodes (with an electrical tension) under the effect of light (See Figure 1.2).

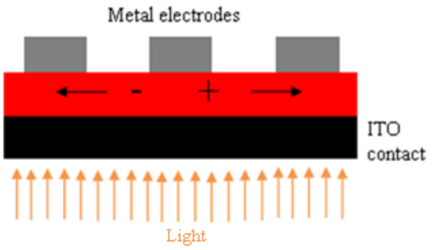

Figure 1.2. Basic operation of solar cells

Finally, the OTFT technology is quite advanced, with devices with a higher efficiency than hydrogenated amorphous silicon, which is the standard material of the TFTs fabrication, used in screens. With a certain voltage tension applied to the gate and to the drain, a controlled current flows through the semiconductor (See Figure 1.3).

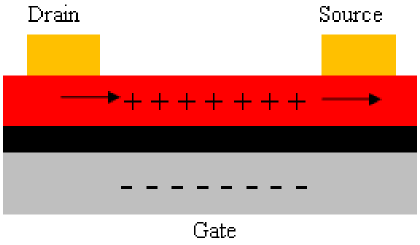

Figure 1.3. Basic operation of OTFTs

Foremost, in this final thesis, the basic concepts such as TFTs, semiconductors and solar cells are defined. Afterward, generalities about manufacturing and measurement methods of OTFTs are specified. Then, concerning the studied samples construction and measurement equipment and the various manufacturing steps are detailed. Finally, the results of the samples analysis and their interpretation are developed.

2 TFT's

2.1 What is a TFT

TFT is the acronym of *Thin-Film Transistor*, which is used to designate the field-effect transistors; it is a special kind of MOFSET (*Metal-Oxide Semiconductor Field-Effect Transistor*), which is composed of several layers of conductive, insulation and semiconductors materials. Therefore, TFT and MOSFET transistors are based on the same operating principle, except that the MOSFET are used for microelectronic applications, while the principal application of TFT's is screens. The term "thin-film" is used to designate thin material layers ranging from fractions of a nanometer (monolayer) to several micrometers in thickness.

2.2 Applications of TFTs

Large-area electronics involves Active Matrix Liquid Crystal Displays (AMLCD) and image lectors [1]. These devices usually require transparent substrates. In Figure 2.1 is presented the pixel structure of colour AMLCD. It consists of two glass panels with liquid crystal substance injected between them. There is a fluorescent light source behind the back panel. First, the light passes through a vertical polarizer and then enters in the liquid crystal substance through transparent conductive electrode (usually ITO[3]). Then the light passes through the second glass plate that has a transparent electrode, common for all the pixels, and after that through color filter. The coloured light can be seen outside. On the back panel there are horizontal and vertical data lines that form two-dimensional address of each pixel. Thin-film transistors (TFTs) are field-effect transistors, used as switching elements between these addressing lines [1][2].

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[3] Indium Tin Oxide

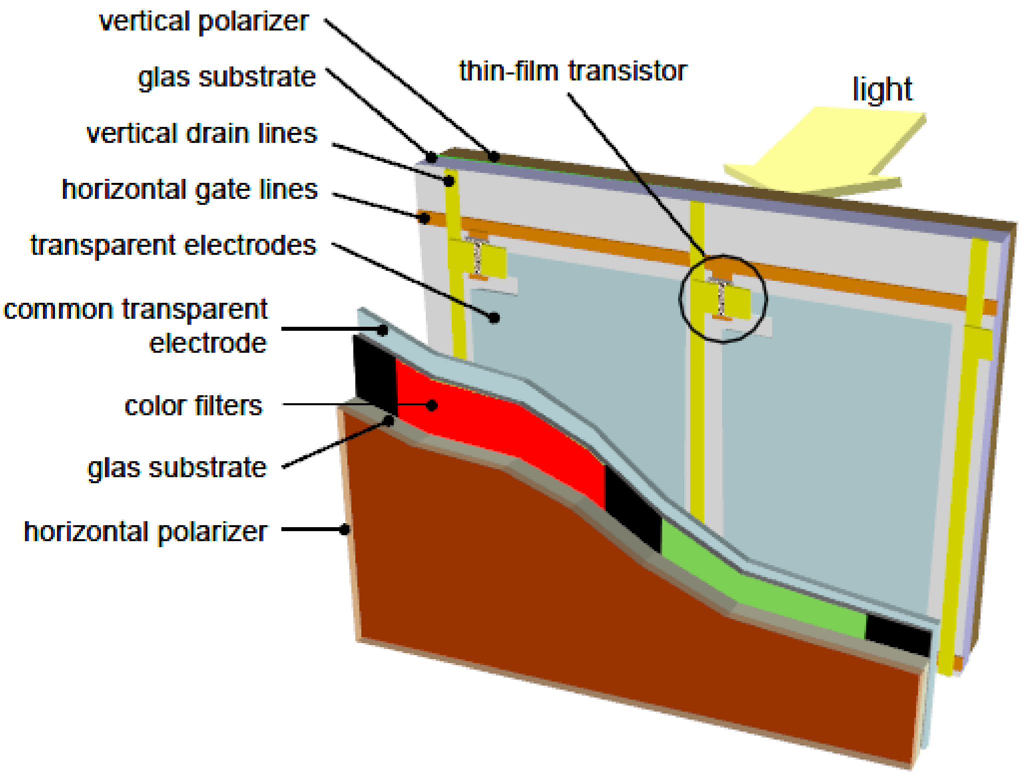

Figure 2.1. Structure of pixel in colour AMLCD (Dosev, 2003)

The role of the TFT is to control the bias between the transparent electrode on the back plate and the common electrode on the second plate, this voltage is applied over the liquid crystal cell. The vertical address lines are connected to the drains and the horizontal lines are connected to the gates of the transistors. When high voltages are applied simultaneously on the drain and on the gate, the TFT is in “ON” state and the drain voltage is applied to the liquid crystal cell. If low voltage is applied on either the drain or the gate line, the TFT is in “OFF” state and no voltage is applied on the liquid crystal cell.

Figure 1.2 describes the operation of the most commonly used twisted nematic liquid crystal cell [3]. When no voltage is applied on the cell (Figure 1.2.a), the liquid crystal molecules are oriented according to the orientations of the two polarizers, which are rotated at 90 degrees each to other. The entering light is polarized by the first polarizer, and then the light’s polarization is rotated to 90 degrees by the liquid crystal molecules. This permits the light to pass through the second polarizer. In this manner, the cell is transparent for the passing light.

On the other land, when voltage is applied on the liquid crystal cell, the liquid crystal molecules are oriented along the electric field (Figure 1.2.b). As the light does not change its polarization, it cannot pass through the second polarizer. Thus, when electric field is applied on the cell, the liquid crystal cell becomes no transparent for the light.

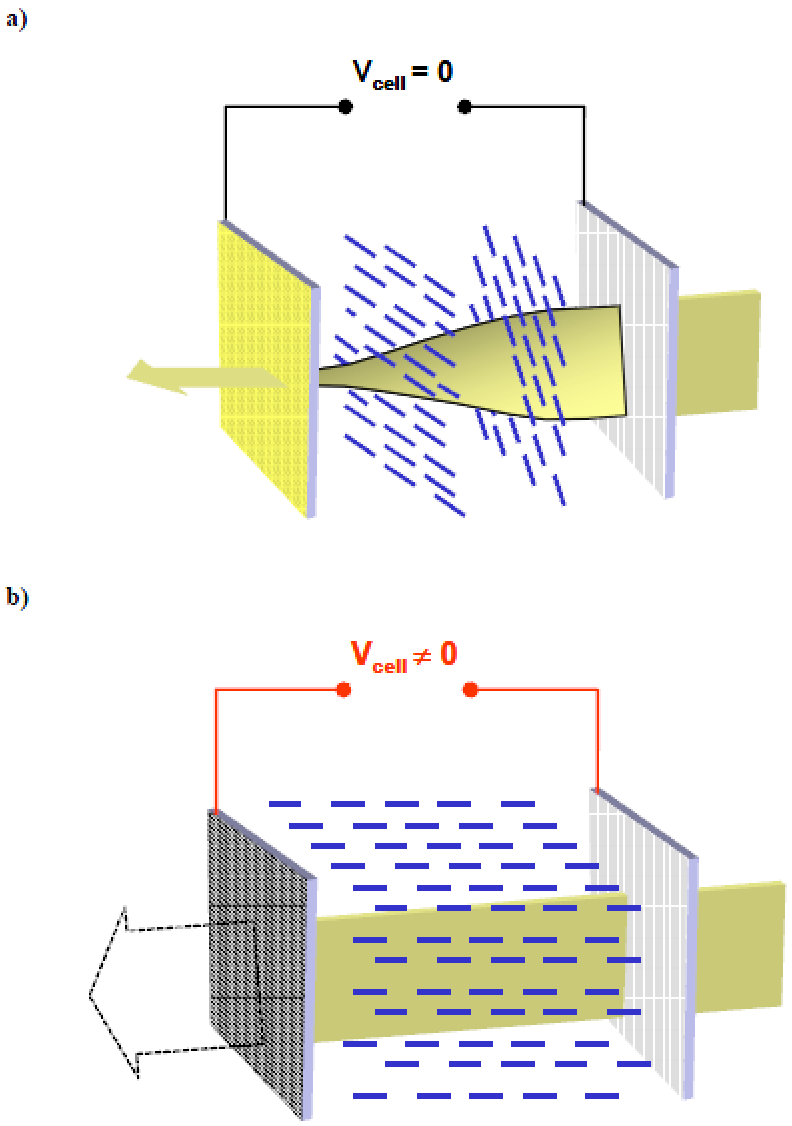

Figure 2.2. Liquid crystal cell operation; a) No voltage applied on the cell; b) Voltage applied on the cell (Dosev, 2003)

TFTs are also studied for solar applications. Indeed, the measurement of TFTs characteristics exposed to light allows us to know if it could be used to make solar cells.

2.3 Composition and types of TFTs

TFTs differ depending on the type of semiconductor that is used and on their physical structure. Regarding semiconductors, most are composed of silicon, i.e. polycrystalline silicon or amorphous hydrogenated silicon (a-Si:H). Silicon has the advantage of the high mobility of charge carriers, which means that it is a good candidate for high frequency applications (especially for polycrystalline silicon). The drawback is price, because we must obtain a crystal structure that can be achieved only at high temperatures. The combustibles using to achieve this adds an ecological disadvantage. An economical alternative is amorphous silicon, this one is easier to achieve because it does not require high temperatures, but the mobility of charges is around 3 times lower. Thus, the amorphous silicon will be the main competitor of organic materials for business applications.

Indeed, organic TFT (OTFT) is an alternative to amorphous silicon as they are ideal for applications requiring large areas, flexibility, low temperature processing and low cost. The mobility of charge carriers in organic molecules and the instability are two of the main concerns of this technology which is booming.

Usually, TFT’s are manufactured by successive layers depositing of insulation, semiconductor and electrodes. The order in which the layers are deposited determines the electrical characteristics of the device. They are strongly dependent on the quality of the top surface and the interface between the semiconductor and the gate insulator. Basically, we can distinguish two kinds of structures: the staggered and the coplanar. As illustrated in the figure below, in the staggered structure (top contact), layers of semi-conductors and insulation located between the drain, source and gate electrodes. By cons, in the coplanar structure (bottom contact), the semiconductor layer is above the drain and source electrodes.

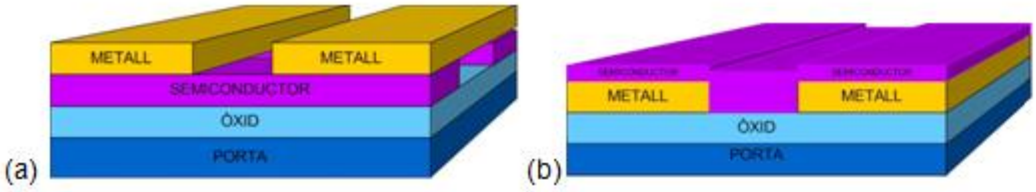

Figure 2.3. Physical structure of the TFT's with (a) staggered structure and (b) coplanar structure.

The staggered structure is more convenient and easier to measure because the drain and source electrodes are over. The coplanar structure, with his contacts at the bottom, is more used when the metal deposit can damage the structure of semi-conductors.

3 Organic semiconductors

A semiconductor is a material that has the electrical characteristics of an insulator, but for which the probability that an electron can contribute to an electric current, though small, is large enough. In other words, the electrical conductivity of a semiconductor is intermediate between that of metals and insulators.

The electrical behavior of semiconductors is usually described using the theory of energy bands. According to this, a semiconductor material has a band gap small enough that electrons from the valence band can easily reach the conduction band. If an electric potential is applied to its terminals, low power appears, driven both by the movement of electrons and that such "holes" they leave in the valence band.

Today, electronics is based on the use of inorganic semiconductors, mainly silicon crystal. The processing technology of crystalline silicon is well developed and the results obtained during the last 40 years have been very spectacular. However, the transformation of crystalline silicon requires very high temperatures and the surface is limited to a few tens of centimeters. Therefore, in the early 80's scientists have undertaken research to obtain a semiconductor that provides solutions to the disadvantages cited above.

The treatment of these new semiconductors, such as hydrogenated amorphous silicon, require moderate temperatures (<300 ° C) and offer the possibility to work on larger areas and on different substrates such as glass and plastic. The hydrogenated amorphous silicon is used among others things in pocket calculators and in the TFT’s of flat screens.

Although organic semiconductors have been studied over the past 60 years, it is only recently that the industry of optoelectronics has made major improvements regarding the efficiency and performance of materials.

Organic materials are based on a structure of carbon atoms. Two main classes can be distinguished: polymers and small molecules. Both have a similar structure, but the main difference lies in the filing process over thin layers.

The nature of the links in the organic semiconductors is fundamentally different than in the inorganic. Organic molecules have intermolecular bonds weaker than covalent bonds specific to inorganic semiconductors like silicon. The consequences of these differences in molecular bonds result in different thermal and mechanical properties, such as a lower melting temperature, lower hardness and, more importantly, a smaller delocalization that has direct effects on the optical and transport charge carriers.

The characteristics of semiconductors that make them popular are:

- Optoelectronic properties that can be changed easily because the molecular structure of these materials can be adjusted.

- They are versatile materials because they have connections that can be broken and their structural defects are manifested by very small forces.

- Because of its versatility, they should not be treated at high temperatures and processes are fairly simple. This allows a lower manufacturing cost and simpler machinery than inorganic materials.

But there are also arguments against these organic semiconductors:

- Organic materials have low conductivity due to the low mobility of the charge carriers ($\mu < 1$ cm ^{2} / Vs), a wide band gap ($E_g > 1.5$ eV), a low doping efficiency and high density of traps.

- Oxidation and reduction reactions occur frequently with certain external agents, which causes defects that cause chemical deterioration of electrical and optical properties.

- The purity of organic materials is low compared to inorganic because purification techniques known and applied to inorganic semiconductors are not applicable to organic. Impurities can act as traps for charge carriers and as doping agent, other undesirable consequences.

3.1 Polymers and small molecules

As mentioned earlier, organic materials used in the manufacture of OTFT can be classified into two groups: small molecules and polymers. The family of the small molecules includes the organic compounds made up of a small number of monomers whose total molecular mass does not exceed 1000amu (atomic mass unit). A monomer is either an atom or a small molecule that has the potential of chemically binding to other monomers of the same species to form a polymer. Consequently, the main difference between small molecules and polymers is the amount of monomers they contain. As small molecule P-type, there are for example pentacene or phthalocyanine, and as we find the N-type fullerene (C_{60}), PTCDI-C13 (N,N'-ditridecyl-3,4,9,10-perylenetetracarboxylic diimide) or PTCDA(3,4,9,10-perylenetetracarboxylic Dianhydrid). Regarding polymers, for example, we have PQT-12 (3,3"-dialkylquarterthiophene), P3HT (3-hexylthiophene) or F8T2 (dioctylfluorene cobithiophene).

A second difference lies in the technological processes used to deposit a thin film. Polymers can be deposited from solution by spin-coating or printing, the small molecule in turn is deposited from thermal evaporation under vacuum, because almost all the small molecules used in OTFT are insoluble. Despite these differences, the physics is behind the small molecules and polymers is very similar, so this final thesis will not make any distinction thereafter. The OTFT studied in this thesis are small molecules, specifically, the samples are composed of semiconductors with p-type pentacene and n-type with the PTCDI-C13. The pentacene is an aromatic compound composed of 5 rings of benzene, it has been extensively studied as a semiconductor for its relatively good stability and its remarkable results in terms of conductivity. PTCDI-C_{13} is also one of the N-type semiconductors that show the best mobility. The structure of some of these semiconductors is shown below on Figure 3.1 and Figure 3.2.

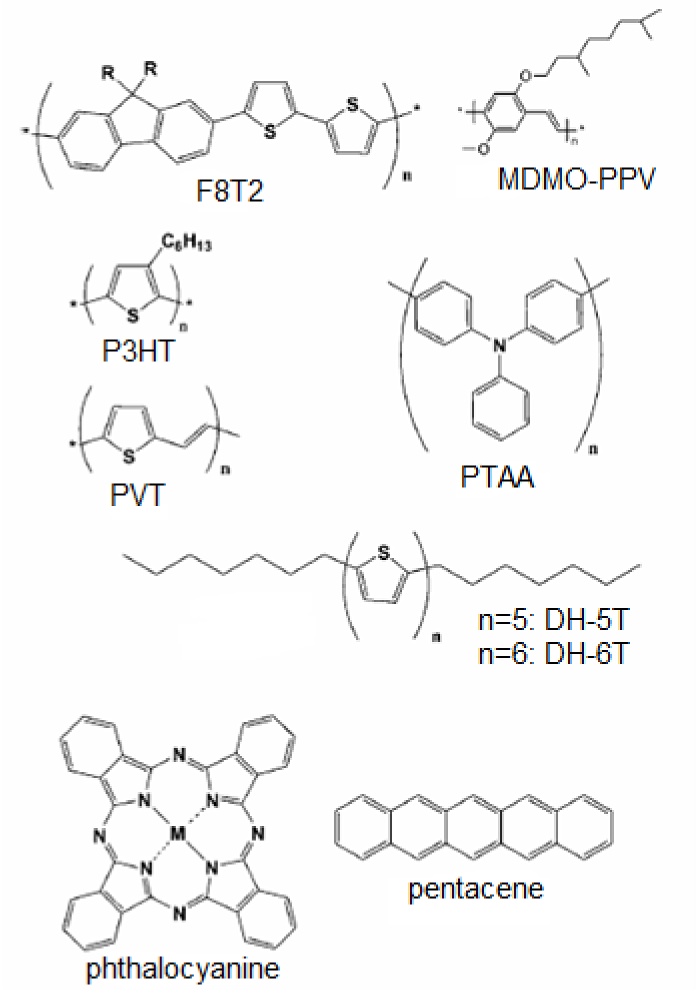

Figure 3.1. Some of the P-type organic semiconductors more used

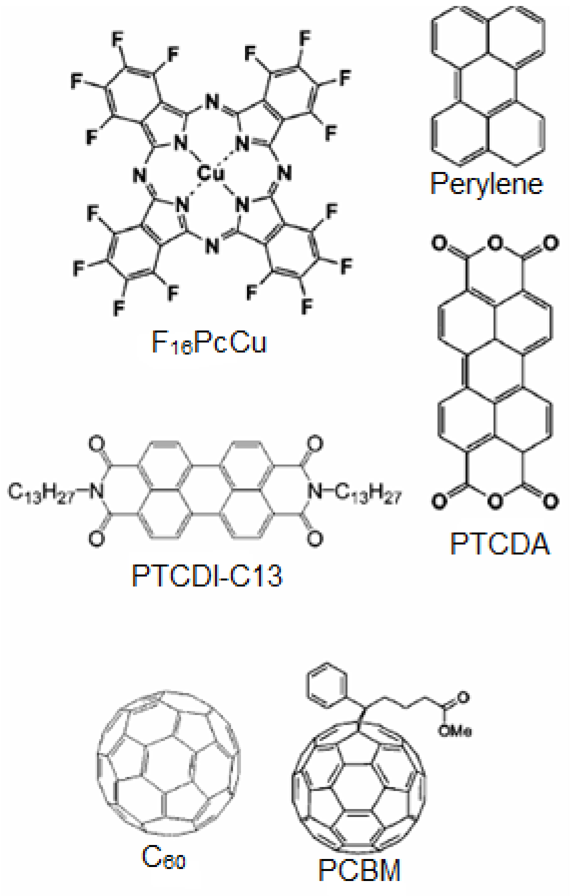

Figure 3.2. Some of the N-type organic semiconductors more used

3.2 Physics characteristics

The semiconductors are carbon based. The carbon atoms have single bonds (which include a pair of electrons) or double bonds (2 pairs of electrons are involved) and this structure allows the properties of semiconductors.

If we look at the most stable configuration of carbon which is $1s^{2}\,2s^{2}\,2px\,2py$, carbon is the chemical element with atomic number 6, normally 2 of these electrons are in condition to form a link because the lowest levels "*s*" of energy are filled (with 2 electrons each). This is not quite right because it is known that carbon can form 4 bonds. This phenomenon is explained by the hybridization of carbon: an electron from the *2s* orbital is excited and moves to the *2p* orbital of higher energy, causing a mixture of *2s* with *2p* orbitals, which form the *sp* hybrid orbital, whose number depends on the molecular structure. In the case of organic molecules, the 2*s* orbital is combined with the 2px and 2py orbitals to form 3 *sp*, known as 3 sp^2, leaving a p_z orbital without hybridization.

Now, the configuration of carbon is $1s^2\ (sp^2)^1\ (sp^2)^1\ (sp^2)^1\ p_z^1$. Note that in the nomenclature, in the sp^2, the "2" refers to the percentage of sp orbital which will be p type (in this case 2 / 3 of p and 1 / 3 s). Two of the sp2 orbitals can form covalent bonds with neighboring atoms, while the third usually form a covalent bond with another carbon atom, known as link σ.

The p_z orbital which has not been hybridized, overlap with the p_z orbital of the neighboring carbon atom and creates a π bond. Thus, we have a double bond between two carbon atoms (σ and π) and single bond between other atoms that can also be carbon giving rise to the conjugated structure [4]. The π bond is significantly weaker than the σ bond and can be easily changed, allowing the electrons to participate in part to conduction.

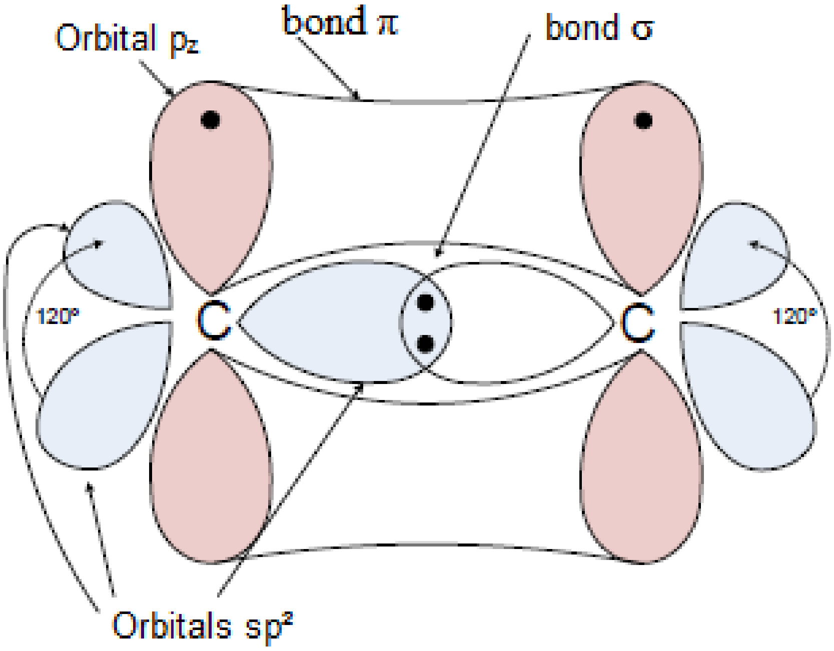

Figure 3.3. Carbon-carbon double bond in organic semiconductor

So, as the inorganic semiconductors we speak of valence band and conduction band to describe the energy levels that electrons must acquire to become a free carrier, for organic semiconductors we use HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital). The highest occupied molecular orbital (or HOMO) is the energy level at the top of this continuous band of occupied states, whereas the lowest unoccupied molecular orbital (or LUMO) is the first available energy level in the unoccupied band.

The bound molecular orbitals (les orbitals moléculaires liées ? *enllaçants*,) are more stable but less energy than unbound molecular orbitals, so if an electron is present in a bond is excited, he can change and occupy an unbound orbital. Carbon, as presented above, forms a double bond with another carbon atom (σ bond and π bond). The π orbital is higher in energy than the σ electrons and can be easily excited to form part of the unbound π * orbital and belongs to the LUMO level, thus creating free carriers. The σ orbitals can be excited at the σ *, which is higher in energy than the π * and therefore will require more energy to break the link.

The energy required to move from a bound to an unbound state depends, among other things, of the interaction energy between the electrons of two atoms. The value of this energy is different for each link. When several atoms are combined, as in any molecular solid, the individual molecular orbital levels broaden into continuous bands, analogous to the valence and conduction bands which arise from band theory with crystalline semiconductors. The more electrons in the system, and the greater their overlap, the broader the bands and the narrower the band gap.

This is the origin of bands in the organic semiconductor and the HOMO and LUMO levels which correspond to the π orbital of higher energy and π* orbital of less energy, respectively.

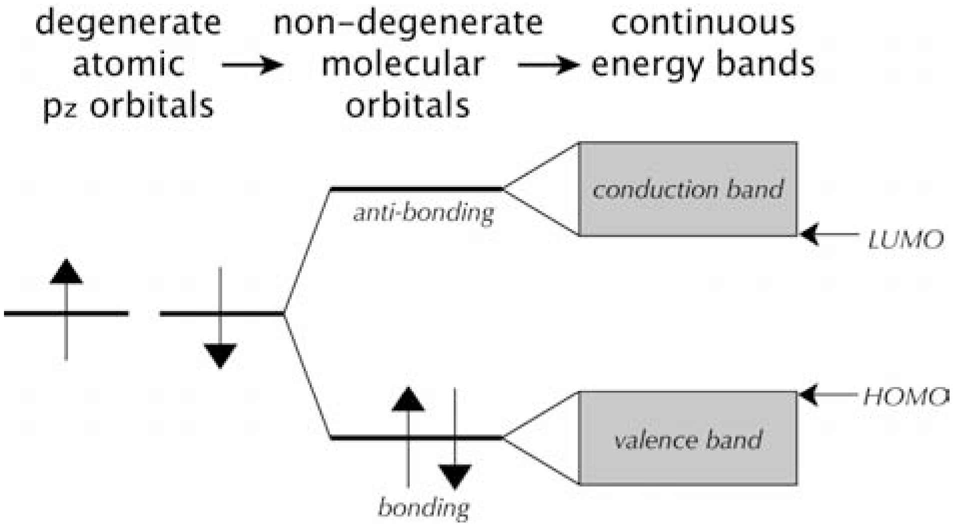

Figure 3.4. Energy diagram, valence and conduction bands (Marsal, 2007)

3.3 N type and P type

To realize stable PN-junctions, the study of the N-type and P-type conducting semiconductor was decisive. The basic principles of doping in organic semiconductors are similar to those in inorganic materials: Mobile carriers are generated by exciting electrons from donors into a conduction band or by capturing electrons with acceptors and thus creating holes in a valence band. In organics, one has to add constituents, which either donate electrons to the lowest unoccupied molecular orbitals (LUMO, n-type doping) or remove electrons from the highest occupied molecular orbitals (HOMO) to generate holes (p-type doping)[12]. The doping operation is very difficult and not yet completely controlled. LUMO and HOMO of organic materials are respectively equivalent of the conduction and the valence band of inorganic materials.

4 Solar Cells

4.1 Conversion of light into current in an organic solar cell

In organic solar cells, molecules are electronically excited by light absorbing. This excitation creates an exciton, what is an electron-hole pair. Because of the low value of the organics permittivity[4], the absorption of one photon creates this electron-hole pair bound by Coulomb forces [7].

The diffusion length of excitons (ie the distance before recombining) is very small, the order of several tens of nanometers. Excitons have to attain the donor-acceptor interface to be separated and create charge carriers (electrons and holes). As the diffusion length is small [8], this implies that the cells have to be very thin. However, if cells are fine, they do not absorb much light, the challenge is to find a balance (see Figure 4.1).

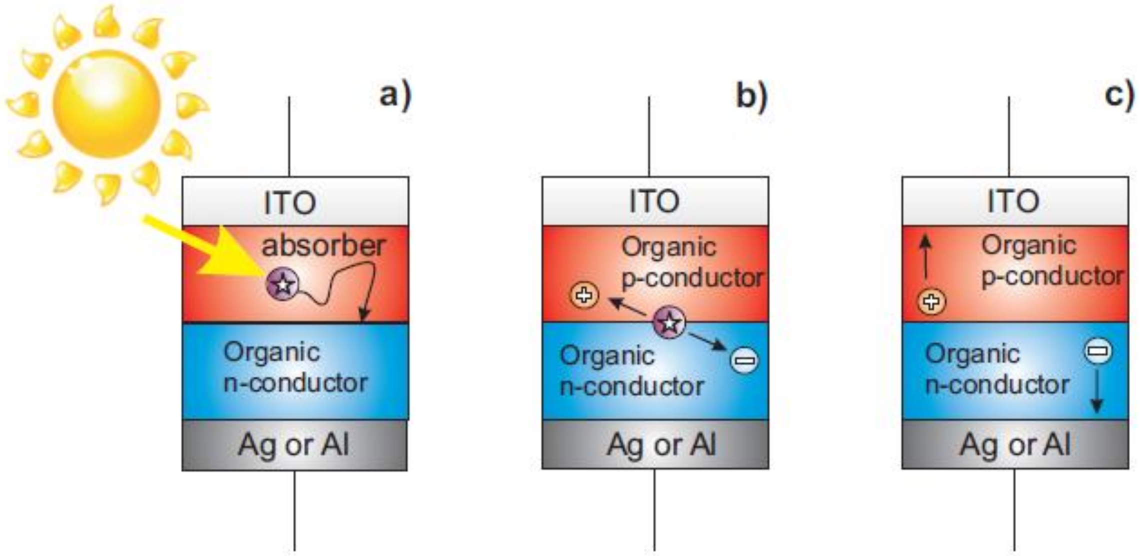

Figure 4.1. Operational principle of organic solar cells: (a) Creation of a Frenkel exciton after light absorption. (b) Exciton diffuses towards a DA-interface where it dissociates into a polaron pair. (c) Diffusion of the charge carriers towards their respective contact electrodes where they can be extracted (Bruder, 2010)

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[4] the measure of the ability of a material to be polarized by an electric field

In classical inorganic solar cells, the bond between the electron and the hole is low because of an efficient electrostatical screening based on quite high dielectric constants ε_r in inorganic semiconductors. Separation and transport to the respective contacts of these charges is made by an electrostatic potential between the two layers of P-type and N-type semiconductors. In the organic semiconductor case, it's a little bit different. The dielectric ε_r is much lower, therefore, the screening of electron and whole is much weaker. Thus, optical excitation of charges is quickly relaxed because of the strong dielectric polarization effects and the binding energies of excitons (E_B) ranging between 0.1 eV and 2 eV [9], what is very high compared to inorganic semiconductors (around 25 meV for GaN for example).

The conversion of light into current in an organic solar cell is taking place in four consecutive fundamental steps: first, light is absorbed and generate strongly bound Frenkel excitons. Secondly, optically activated excitons are dissociated but still bound positive and negative charges (generation of electron-hole pairs). Then, transport of electrons and holes from the bulk of the device to the respective collecting electrodes. Finally, charges carriers are extracted at the electrodes.

To overcome the binding bound of organic semiconductors under ambient conditions, the interfaces donor-acceptor (DA) had to be introduced. Indeed, the exciton diffusion length L_D is usually shorter than the sample thickness and the strongly bound Frenkel excitons have to be countered [12].

4.2 Donor-acceptor (DA) interface

A donor can be described as a molecule which transfers an electron to another molecule over an interface in a donor-acceptor system, and which acts as an organic N-dopant and donates an electron into the LUMO of an organic semiconductor. The characteristics of organic acceptors can be summarized similarly [12].

The exciton dissociation is energetically favorable if the difference of energy between the ionization potential IP_D of the electron donating material and the electron affinity EA_A of the electron accepting material is larger than the exciton binding energy E_B or exciting energy E_{exc} (see Figure 4.2 and Figure 4.3).

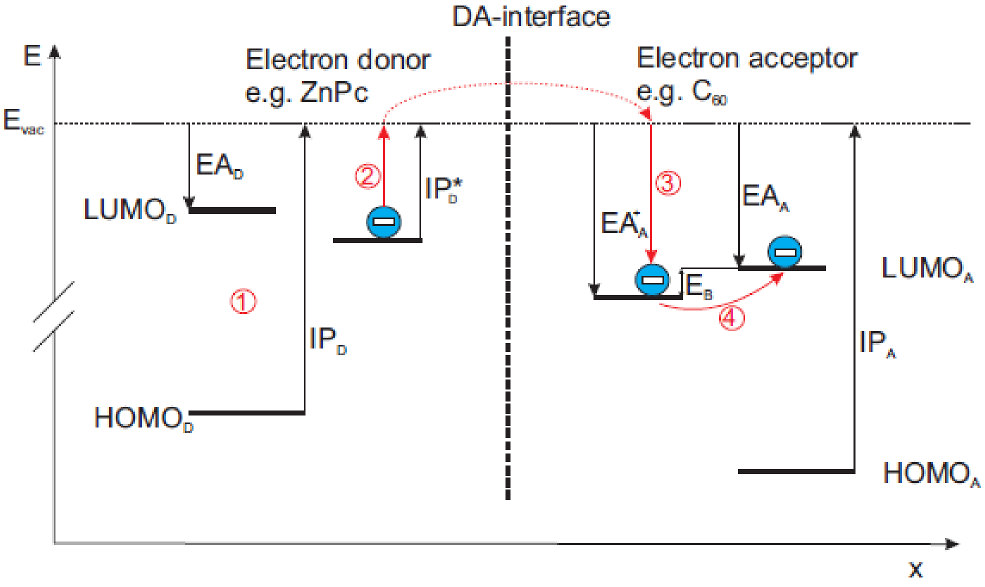


Figure 4.2. Schematic picture describing the exciton dissociation at a DA-interface: (1) $HOMO_D$ and $LUMO_D$ level of an uncharged not excited donor molecule. (2) An excited donor molecule is ionized by an energy IP_D*. (3) The electron is transferred ultrafast to the LUMO of an electron acceptor within a sub picosecond timescale by gaining the energy EA^+_A. (4) Due to the Coulomb interaction between the electron on the acceptor and the remaining hole on the ionized donor, an additional energy barrier E_B has to be overcome for a spacial separation of the charge carriers. Thus, exciton dissociation is energetically favorable if IP^*_D-EA_A < E_B. (Bruder, 2010)

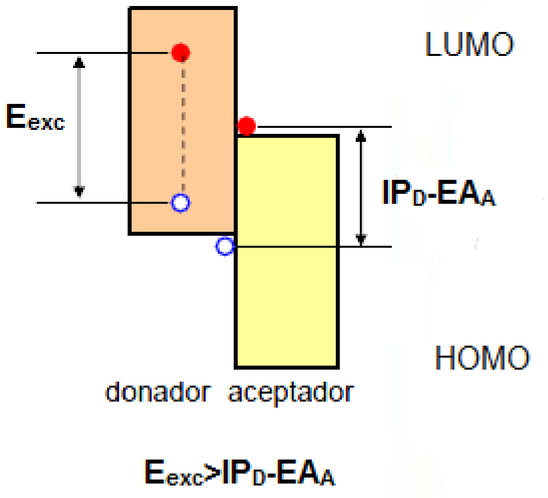


Figure 4.3. Schematic illustration of the energy level alignment requirements for efficient charge transfer. The energy levels diagrams for donor-acceptor heterojunction are shown

IP^*_D is the ionization potential of the excited donor, EA_A the electron affinity of the acceptor and E_B the binding energy (or exciting energy E_{exc}) of the excitons in the donor, in absolute values. When the exciton is dissociated, electrons are transferred on an acceptor molecule and holes stay on a donor molecule. Electron and hole are spatially separated but even though these charge carriers reside on two distinct molecules which lead to a lowered recombination rate (with a life time from micro to milliseconds) as compared to the Frenkel excitons (with a lifetime around nanoseconds), the two opposite charges are still Coulomb bound. Consequently, an additional step is necessary for the completely pair dissociation.

4.3 Charge carrier separation in organic heterojunction solar cells

An electric built-in field is needed to overcome the Coulomb attraction between electron and hole because they are spatially separated but still bound. The internal field has to be enough large or there will be a high probability of charge recombination, this field depends principally on the work functions of the metal electrodes. If the field is able to separate the charge carriers, holes and electrons can be transported towards their respective contacts and generate a photocurrent. The layer thickness of the absorbing material is the limiting factor in heteronjunction. To absorb a large part of the incident light, the layer thickness of the absorbing material has to be more or less the same than the absorption length (around 100 nm) [12].

5 Fabrication of OTFT’s: generalities

The organic semiconductors are not able to compete with inorganic semiconductors regarding electrical properties; one of the major goals of technology is to achieve organic produce devices at a reduced cost. According to this idea are developed deposit techniques very fast and cost-effective for a mass production.

The manufactures of TFT using polymers or small molecules are slightly different but have the same steps: purification of organic matter, deposition of dielectric material (Al_2O_3 in this project) on a conductor substrate (TFT gate), semiconductors deposition and electrodes deposition (source and drain). The order in which steps are performed depends on the physical structure of the TFT.

Thanks to the good mechanical properties and to the simplicity of the deposition process of organic semiconductors, the OTFT can be fabricated on any substrate which is sufficiently flat. For convenience, and especially in the experimental, usually the crystalline silicon is used as gate electrode.

Below are detailed the different deposition stages: dielectric, semiconductor and electrodes.

5.1 Deposition of dielectric

The insulation is often composed of silicon oxide (SiO_2) due to its outstanding dielectric properties, this component is well known in the microelectronics field. Silicon oxide can be obtained by thermal oxidation; it is a chemical reaction between the silicon and oxidizing substance, usually oxygen (O_2, called dry oxidation) or steam (H2O, called oxidized wet). To facilitate this reaction, the reaction is performed in furnaces with high temperatures in the range of 800-1100 °C depending on the thickness and the speed that we want to achieve. If the goal is to manufacture devices on flexible substrates, the dielectric has to be deposited at lower temperatures but the SiO2 cannot be used because it requires high temperatures.

There are a lot of researches dedicated to dielectrics that can be deposited at low temperature (< 200°C). Some of these dielectrics are polymers that are deposited by spin coating, such as PMMA or PS. In recent years has appeared a new technique that allows the deposition of inorganic dielectrics at low temperature. This technique is called ALD (Atomic Layer Deposition). This allows, among other things, the Al_2O_3 deposition, used in this project.

5.2 Deposition of organic semiconductors

An important difference between polymers and small molecules is how thin layers are deposited. While layers of small molecules are deposited from the gas phase because it has good stability and it has low molecular weight, polymers are deposited from solution.

The order and the manner to deposit polymers or small molecules on a substrate depends on the properties of the substrate surface. Like this, it was found that by placing a thin layer, a monolayer made of the material, we can control the properties of the layers deposited above.

5.2.1 Deposition techniques of small molecules

Vacuum thermal evaporation (VTE) is the most popular form of deposit of organic material (see Figure 5.1). The process involves the sublimation of a compound which is located in a small bowl inside a vacuum chamber, on a substrate. The vessel containing the compound must be resistant to heat that can be can be easily made by electrical current in a resistance. Normally, evaporation occurs in one direction by a sort of chimney. As evaporation occurs, the molecules can travel evaporated under vacuum in the container substrate directly without touching the walls of the room. The substrate is placed above the source, this way it avoids that particles of dust or residues of the room to fell on the sample.

The deposition rate at which molecules are deposited on the substrate depends on the speed at which they are able to escape the solid state, that's why the transit time between the container and the substrate should be minimal. One way to manage the pace of deposition is to play on the temperature of the container. Besides that, most of the material deposited may be controlled by a shutter, it’s a surface that is positioned between the source and the substrate. Like the beam of evaporated material is directional, if we block the path of the beam there will be a minimum direct deposit or practically nil. A quartz sensor informs us about the thickness of the material that has been filed, simply close the shutter when it has reached the desired thickness [5]. This deposition technique is used in this project to deposit pentacene and PTCDI-C_{13} (see deposit characteristics in Chapter 8.2 Organic semiconductors deposition8.2).

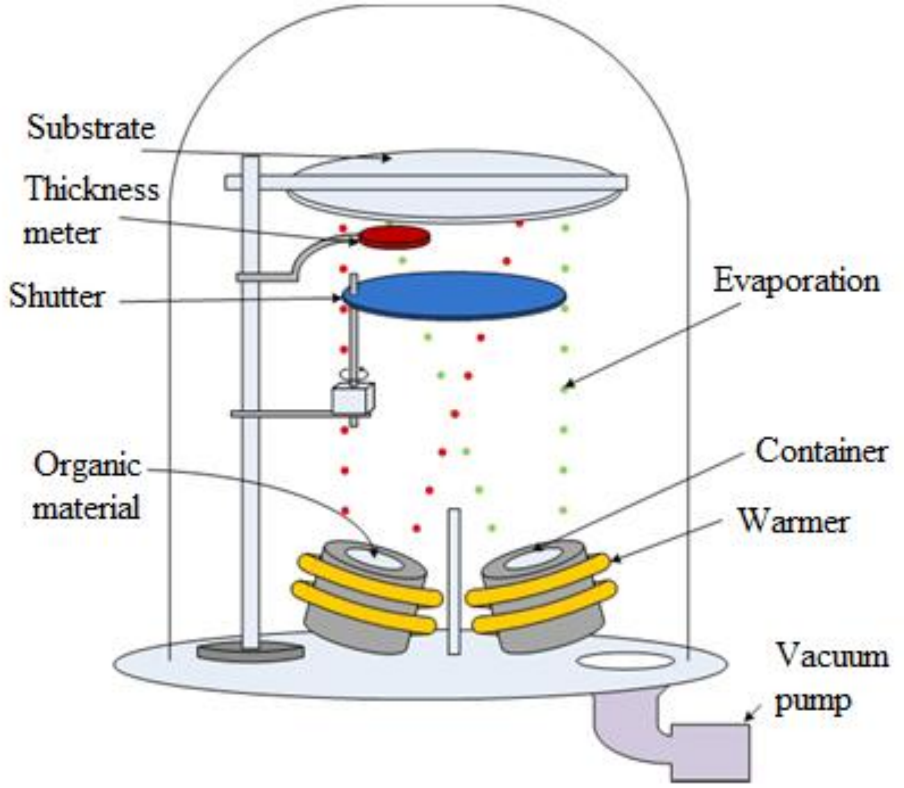


Figure 5.1. Diagram of vacuum thermal evaporation (VTE) (Marsal, 2007)

Organic vapor phase deposition (OVPD): based on a principle similar to thermal evaporation, but it improves certain aspects (see Figure 5.2). In this case, an inert gas is used to be transported by convection organic molecules to the substrate surface which is at a temperature low enough to condense the compound organic. The thermal evaporation have difficult to ensure uniformity in the thickness of the deposited element, another problem was that much of the material evaporated cover the walls of the room because they are colder, which may give rise to pollution problems by impurities. In OVPD, the walls are heated to avoid this problem. Needless to say that this warming is done so that the chamber has a thermal gradient which promote convection [6].

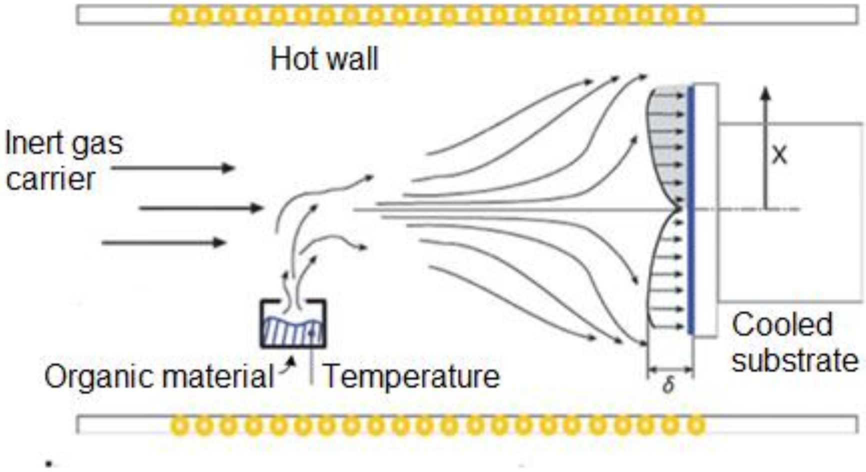


Figure 5.2. Basic principle of organic vapor phase deposition (OPVD) (Marsal, 2007)

5.2.2 Deposition techniques of polymers

To deposit polymers, it is necessary that they have been previously dissolved in a solution. Note that some of these techniques can also be used to deposit small molecule when they are soluble.

Spin-coating: depositing a small amount of organic material in liquid form on the substrate rotating with a speed of 500 to 10000 rpm. During the process, a solid layer is formed due to the flow and the evaporation of the fluid. The desired thickness is controlled by the rotational speed and the initial concentration deposited on the substrate.

This is not a precise technique, but it is economical and easy to implement. It has indeed some drawbacks for the deposition of the layers because the solvent used must not damage the lower layers. The speed of rotation, the substrate temperature and the solvent will determine the nature of the links in the polymer chains.

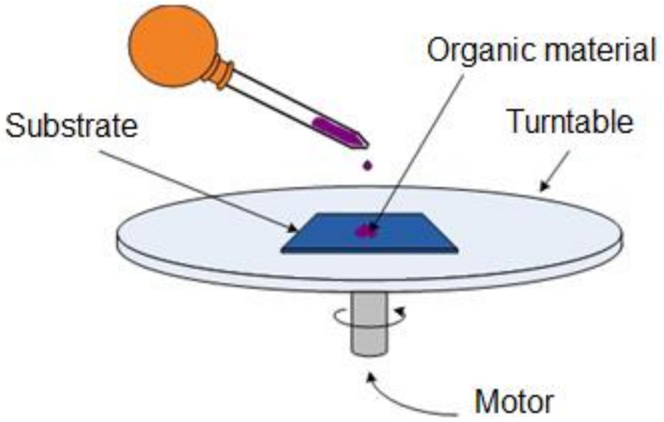


Figure 5.3. Basic outline of the deposit to spin-coating (Marsal, 2007)

Inkjet printing: a method of depositing droplets (pico-liters) of organic materials on a substrate in the same way as conventional ink printers. There are different techniques: creating controlled size droplets of organic compound through a hole, bubbles are created by the piezoelectric actuator or material heating, then it is used sound waves to break the surface tension and thus expel droplets. This technique is rather intended to create patterns for a large-scale manufacturing of devices, but it has disadvantages such as poor resolution, due to the impact of drops on the substrate or the possible incompatibility with the print head solvent or underlying layers.

Organic vapor jet patterning (OVJP) is a very effective method with a good resolution to make the deposit of organic semiconductors on the TFT. It is based on OVPD: grab a hot molecule gas of inert molecules in the vapor of the organic compound, later expanded to a microscopic nozzle that produces a beam at high pressure and low temperature where are absorbed only the organic molecules.

Screen Printing: Using a rubber brush, a dough of the organic compound is deposited by a template on a substrate. So the form of the template will define the shape of the semiconductor.

Gravure printing: a roll pre-impregnated with the design running on the surface of the substrate by transferring the design.

Dye-sublimation: an image is transferred from a donor to a substrate by applying localized heat usually supplied by laser to obtain a better resolution.

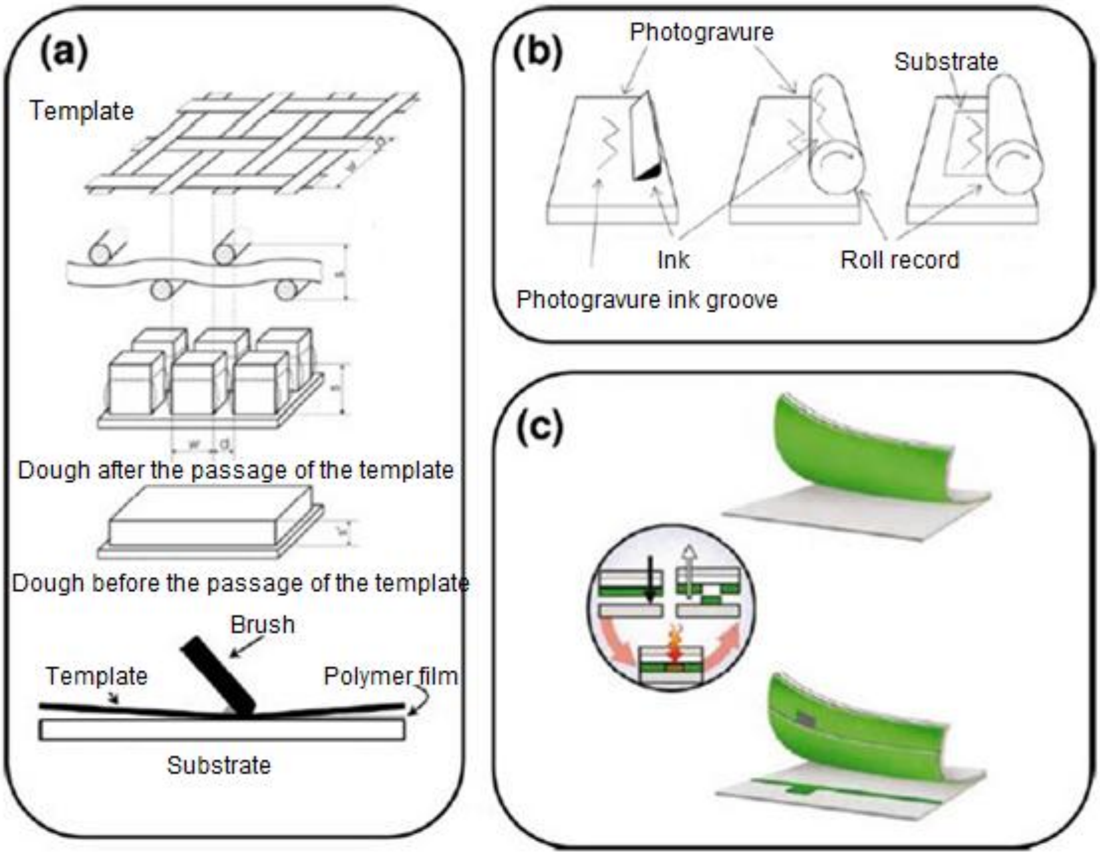


Figure 5.4. Methods to define paths : (a) Screen printing, (b) gravure printing, (c) dye-sublimation

5.3 Deposit of electrodes

Depending on the material used as electrodes, different deposition techniques can be used.

VTE: the oldest technique is to heat the tank and equipment conductors (gold, aluminum, etc.) in a container until it melts and evaporates. The vapor condenses on the surface of the substrate and covers a certain area with the metal. All this is done under vacuum so as not to alter the motion of the atoms in its path. The substrate must be at a sufficient distance from the heat source as high temperatures may also evaporate the organic material. To get the desired shape only put a mask on the substrate.

Sputtering: the material deposited does not pass through the liquid phase, ions from a solid block are torn off with an inert gas (usually argon) accelerated by an electric potential. The atoms of the material will settle on desired surface. This technique is useful when the electrodes are composed of several metals (aluminum silicon and copper, for example) for which the thermal evaporation is done at different temperatures for each compound. In this case there is an ion bombardment on the substrate. This bombardment is used to have a better layers grip. However, this is not a suitable technique for the deposition of metals on organic materials such as ionic bombardment degrades organic materials.

Sometimes, polymers are used as electrodes: the use of PEDOT (poly (3,4-ethylenedioxythiophene)) is appropriate because it has good conductivity, flexibility, synthesis and environmental stability. The polymer can be deposited by one or other of the techniques described in the previous section.[2]

5.4 Purification of organic materials

The standard methods used in the purification of organic materials reach seldom more than 99.9% of purity. This level is insufficient, because the impurities can greatly reduce mobility by acting as traps for carriers.

Some of the techniques used in the purification of small organic materials molecule are:

- Chromatography: This technique involves passing the compound in liquid or gas phase through a stationary material. Purification is based on the difference of affinity between stationary equipment and compounds present in the solution

- Refining by zone-floating: the solid compound to be refined is shaped bar. The bar moves longitudinally in a hot and very localized area. This melts the compound and the dissolved impurities move to the end of the bar.

- For chemical reactions: when impurities are strongly linked to a material or when they are not distinguished by physical methods of purification, chemical compounds can turn dirt into compounds easily separated.

6 Electrical characteristics of OTFTs: generalities

To understand the OTFT characteristics, it is useful to know how operate the MOSFET (also known as the abbreviation MOS) because the characteristics are similar and the reasoning of its working as well.

The transistor is widely used in electronics and particularly in digital electronics. It was designed in the 30s but his production began to spread in the 60s. Two decades later, appeared the first OFETs (MOS transistor with organic semiconductor), with which we obtained best results in efficiency in the understanding of physics in the understanding of its functioning.

There are two main types of MOS transistors: the NMOS (MOS transistor with N-channel) and the PMOS (MOS transistor with P-channel). They are composed of three electrodes (sometimes 4): G (gate), D (drain), S (source), and Sometimes B (Bulk). The gate is isolated from the others by a dielectric, forming a plate capacitor. If we speak about a NMOS transistor, the bulk or substrate is composed of a semiconductor doped P, the drain and source are N-type (generally heavily doped for ohmic contacts) and the gate is metal or silicon heavily doped polysilicon. In the PMOS case, drain, source and volume have an opposite dopage. The following figure shows the classic pattern of an NMOS transistor.

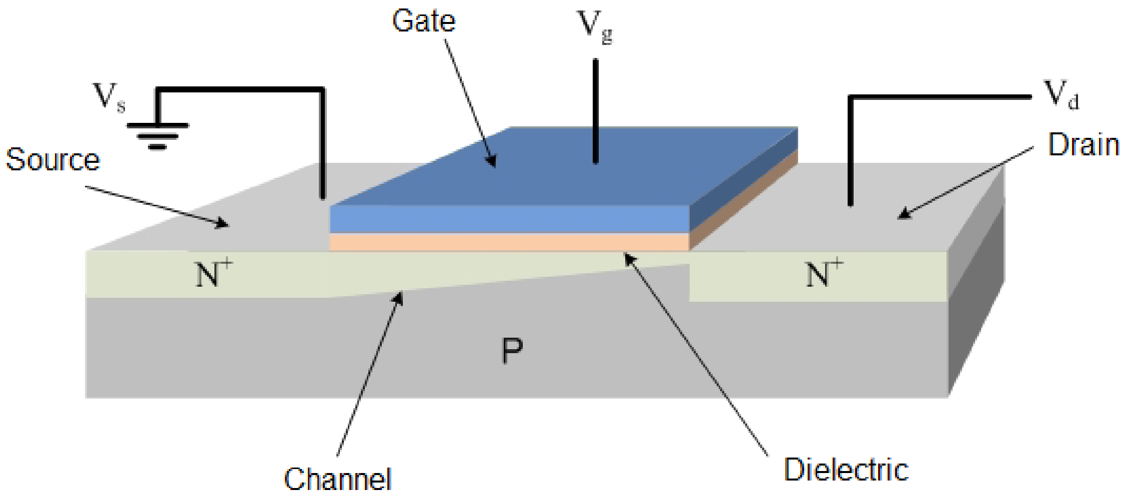


Figure 6.1. Diagram of an N-channel MOSFET

Depending on the voltage applied to the gate, the MOSFET has three functioning possible (example of a N-channel MOSFET):

- Without gate polarization ($V_G = 0$ V), conduction is not possible between S and D because there is no conduction channel formed, the transistor is turned off. The PN junctions that make up the volume with these two electrodes (D and S) are reverse-biased, as two opposing diodes. We say in this case that we are in an open circuit.

- When the polarization is negative ($V_G < 0$ V) there is an accumulation of holes by capacitive effect in the area near the oxide, making it more p-type. The situation is even worse than before. They say that we are in accumulation mode. While the current between drain and source should ideally be zero when the transistor is being used as a turned-off switch, there is a weak-inversion current.

- With a positive gate tension ($V_G > 0$ V), the transistor is turned on, there is an accumulation of electrons just below the oxide (see Figure 6.2). So, a N-channel has been created which allows current to flow between the drain and the source. The MOSFET operates like a resistor, controlled by the gate voltage relative to both the source and drain voltages. Henceforth, we shall consider only this mode of operation since this one is more interesting.

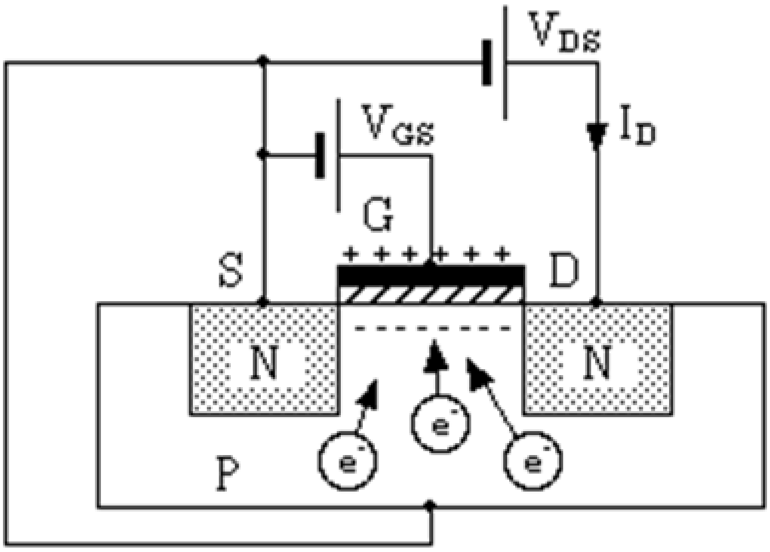


Figure 6.2. Electrons accumulation on the dielectric-semiconductor interface with positive Gate tension

In reverse mode doing a qualitative analysis of the unit operating, the higher the voltage applied to the gate, there will be more accumulated electrons in the channel and the resistance will be less important between the drain and source. In this way, there is a linear increase of current between the source and drain (I_{DS}), the same result will be achieved if we increase the tension between these two electrodes (V_{DS}). This work area is called the ohmic region.

Now, in the case of $V_G > V_t$ and the the V_{DS} value is gradually increased. If the source is connected to earth (ground), along the way there will be a potential distribution: there is a side which is the drain voltage V_{DS} and the other side the source which is zero potential. The potential difference between the gate and various points in the channel will be uneven along this channel. Thus, the area close to the source will be V_G and those close to the drain will be V_G - V_D. If this potential difference is not greater than V_t in all respects between the drain and source, the channel will be reduced and can simply disappear. Even in this case the electrons can move because the PN junction in reverse (P and N in the volume in the drain) generates an electric field that helps electrons to cross. In this situation, the current ceases to increase (first approximation), and remains constant when the voltage V_{DS} increases. We are now in the saturation operating zone.

With a PMOS transistor, the voltage applied to the grid will be negative to attract holes in the N-type area. These holes will be in contact with the drain and source electrodes, where the material will be P-type in this localized area. The holes move towards the drain to be polarized more negatively than the source.

Organic FETs have thin films structures (TFT) because it's more suitable when materials with low conductivity are used. The OTFTs are structurally similar to the MOSFET, but with some variations: the order of manufacturing steps is different and the source and drain electrodes are metallic instead of using doped semiconductors.

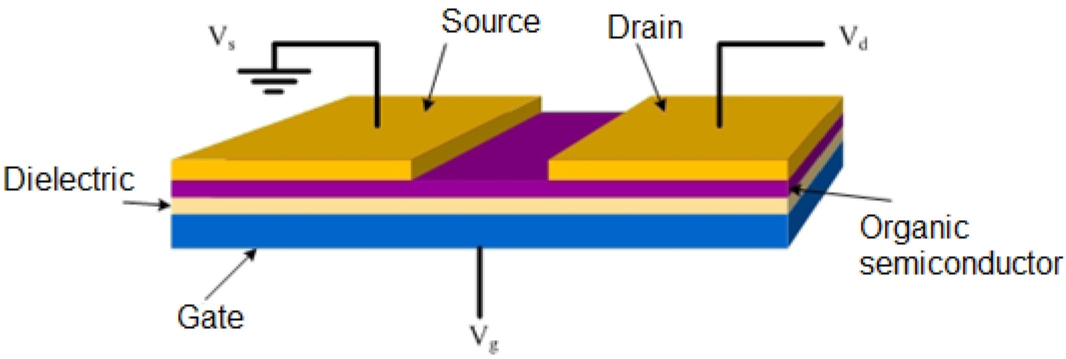


Figure 6.3. Diagram of an OTFT with top-contact structure

The concept of doping is conceptually different for organic or inorganic semiconductors. In the inorganic semiconductor, a N or P-type is obtained by implanting impurity acceptors or donors in a substrate which in principle could be intrinsic. In organic semiconductors the current concept involves two criteria:

- The first says that there is a P or N-type when the substrate has more facilities to transport holes or electrons, ie when moving from one type of charge carrier is greater than another.

- The second criterion refers to the injection of the charge: it is said that a semiconductor is P or N-type, when you can easily inject holes or electrons, respectively. That looks the metal used as electrode and in short, its work function [6].

Unlike MOSFETs, the organic transistors work in accumulation mode. Indeed, applying a negative gate voltage (V_{GS} <0) in a P-type transistor, it leads to an accumulation of holes near the interface between the insulator and the semiconductor which can form a channel of low resistivity between the electrodes (note that in the case of the MOSFET, the gate polarization causes inversion mode) Applying V_{DS} <0, it allows current to flow through the channel. Basically, the device leads when V_{GS} <0 and the current begins to flow when the voltage applied to gate is very low. The voltage at which the current begins to flow is called the threshold voltage V_t.

Basically, the device leads when Vgs <0 and the current begins to flow when the voltage applied to gate is very low, the voltage at which the current begins to flow is called the threshold voltage Vt. Strictly speaking, the concept of threshold voltage is not applicable to these devices, since it refers to the mode of inversion MOSFETs, but qualitatively expressible as the gate voltage for which the resistivity of the channel has a specific value.

As mentioned previously, although the operation of OTFT does not follow that of the MOSFET, we use the same terms to represent the current between the electrodes. Thus, when an OTFT is in the ohmic region (V_{GS}-Vt> V_{DS}), this means that the channel is not fully trained in all issues and that the current flowing is:

$$I_{DS} = \frac{W C_{ox} \mu}{L}\left(V_{GS} - V_t - \frac{V_{DS}}{2}\right) V_{DS}$$

Equation 1

Where L and W are the length and width of the channel, respectively, C_{ox} is the ability of the oxide used per area unit and μ is the mobility of charge carriers. When we enter in the saturation zone (V_{GS}-V_t <V_{DS}) we consider that the channel has points that are in the strangulation and the current that flows will remain constant (in first approximation) when increase electrodes voltage. Qualitatively, we can say that the channel becomes increasingly resistant as V_{DS} increases. This saturation zone begins when V_{DS} = V_{GS}-V_t and replacing this expression equal to Equation 1, we obtain:

$$I_{DS} = \frac{W C_{OX} \square}{2L}(V_{GS} - V_t)^2$$

Equation 2

At this time, the work areas of the transistor are well defined and we know how it works. It remains to know how to interpret the actual graphics for the settings that interest us.

6.1 Output characteristic

The output characteristic of a transistor is used to observe the behavior described in expressions Equation 1 and Equation 2. To do this, we measure the current flowing through the electrodes with the voltage V_{DS} of a series of consecutive points starting with the value for which there is no conduction to the value where there is saturation. This measure is repeated for different gate voltages so that we can see how the transistor changes operating area near of $V_{DS} = V_{GS}-V_t$.

The fact that the transistor is saturated indicates that what is measured is effectively the trace of a transistor because we could have problems of short-circuits or unwanted contacts between the resistive electrodes, which is visible in the saturation zone.

Looking at the Figure 6.4, when V_{DS} is small, we can say that the characteristic is almost linear and the Equation 1 can be written as:

$$I_{DS} = \frac{W C_{OX} \mu}{L} (V_{GS} - V_t) V_{DS}$$

Equation 3

If the derivative of I_{DS} on the derivative of V_{DS} is made, we get the channel conductivity or resistance following:

$$R_C = \sigma_C^{-1} = \frac{L}{W C_{OX} \mu (V_{GS} - V_T)}$$

Equation 4

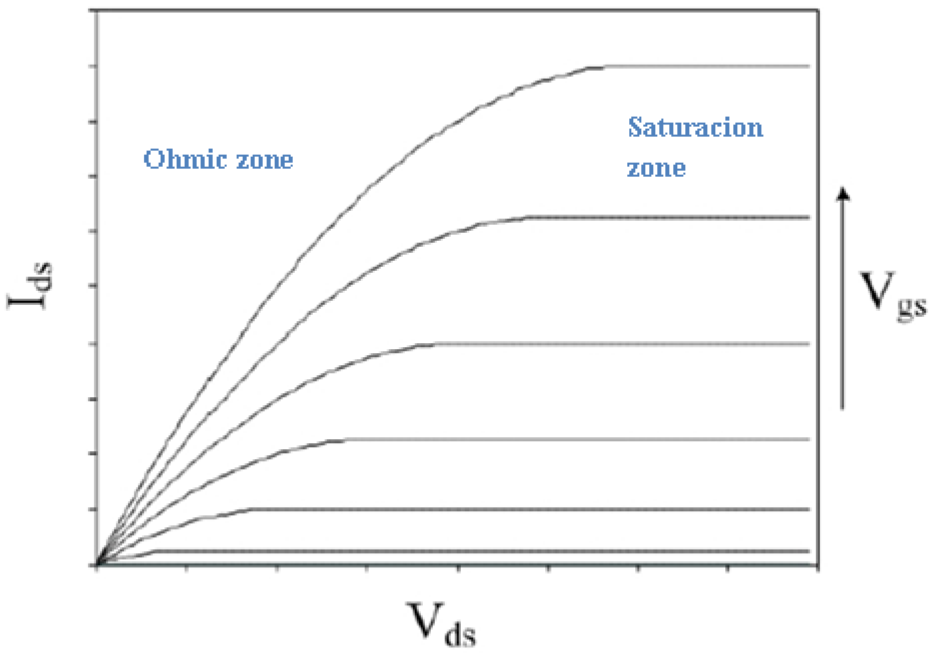


Figure 6.4. Output characteristics

6.2 Transfer characteristic

The transfer characteristic is obtained by measuring the I_{DS} with the voltage applied to the gate (V_{GS}) when is applied a fixed voltage V_{DS} between the electrodes. If the potential difference between source and drain is high enough, you can see how current increases with an exponential trend as indicated by the Equation 2, after the curve becomes linear. Indeed, as the channel conductivity depends on the voltage applied between the gate and the channel:

$$\sigma(x) = \square Q_C(x) = \square(V_{GC}(x) - V_t)C_{OX}$$

Equation 5

And the current depends, in a simplified manner, on the conductivity and the voltage between the electrodes, $I_{DS} = K.\sigma.V_{DS}$ in saturation zone and it is considered that $V_{DS} = V_{GS}-V_t$. It can be said that the current increases exponentially with gate voltage according to Equation 2.

One of the observable characteristics with the transfer graph is the relation I_{on}/I_{off} which determines the transistors properties when they are used as switches. With a P-type transistor: when a negative V_{GS} is applied, there is an accumulation in the channel and conduction is achieved between the electrodes, which is not generated when V_{GS} is positive. The graph shows us their ability to accumulate both types of charge carriers. In this P-type transistor, for example, when I_{on} is larger, it's easier to accumulate holes and when I_{off} is smaller it is harder to accumulate electrons. In applications such as LCDs, this property could be an indication of the contrast that can be offered.

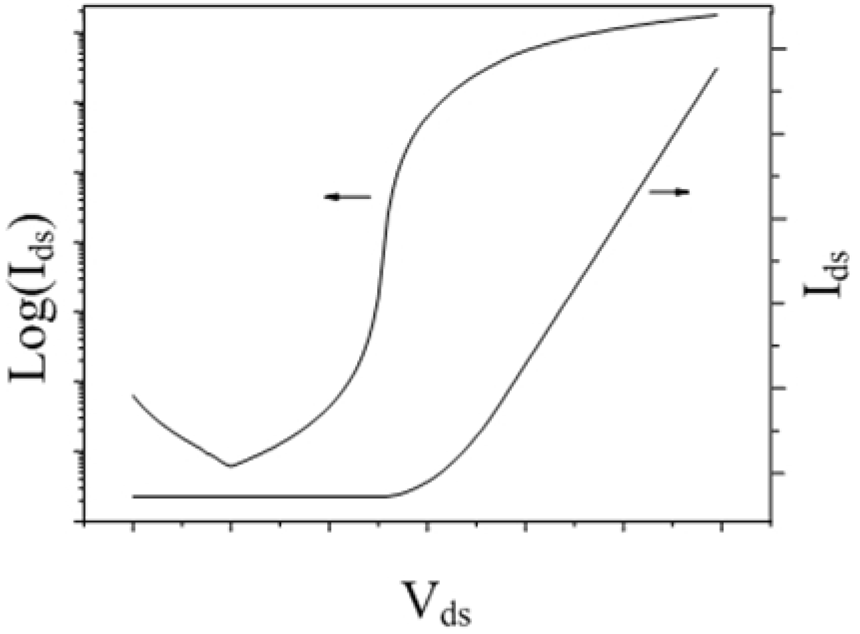


Figure 6.5. Transfer characteristic

With transfer graph, from the transconductance, it is obtained the carriers mobility in the ohmic zone (with constant V_{DS}):

$$g_m = \frac{\partial I_{DS}}{\partial V_{GS}} = \frac{W C_{OX} \mu V_{DS}}{L}$$

Equation 6

The carriers mobility will be calculate from the saturation characteristic.

As seen on the graph, the transconductance valor is not constant, consequently the mobility either, which depends on the gate voltage.

6.3 Saturation characteristic

If the gate and drain are polarized the same voltage, it is sure that the transistor remains in the saturation zone. To achieve the saturation characteristic, the current I_{DS} is measured by a series of tensions where $V_{GS} = V_{DS}$, where the curve will pass from the non conduction to a high conduction ($|V_{GS}| > |V_t|$). This will result in an exponential characteristic as described in Equation 2, which can be modified to remove some parameters.

$$I_{DS} = \frac{W C_{OX} \mu}{2L} (V_{GS} - V_t)^2$$

$$\Rightarrow \sqrt{I_{DS}} = \sqrt{\frac{W C_{OX} \mu}{2L} (V_{GS} - V_t)^2} = \sqrt{\frac{W C_{OX} \mu}{2L}} . V_{GS} - \sqrt{\frac{W C_{OX} \mu}{2L}} . V_t$$

Equation 7

$\sqrt{I_{DS}}$ is fixed to obtain a line like $y = Ax - B$:

$$A = \sqrt{\frac{W C_{OX} \mu}{2L}} , \qquad B = \sqrt{\frac{W C_{OX} \mu}{2L}} . V_t , \qquad x = V_{GS}$$

So the mobility and the threshold voltage can be found:

$$\Rightarrow \mu = \frac{A^2}{\frac{W C_{OX}}{2L}}$$

Equation 8

And $V_t = \frac{B}{A}$

Equation 9

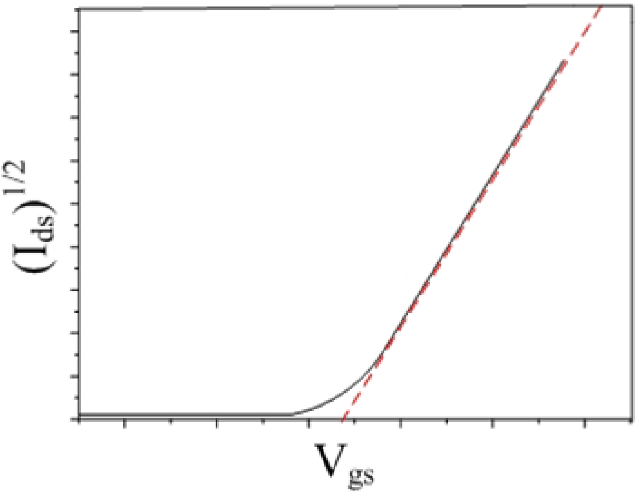


Figure 6.6. Saturation characteristic

It is possible to not know the tension V_t. In this case the observation of the saturation graph allow to calculate the A and B parameters for an posterior area of the elbow (on the chart) to ensure that we are in an full conduction area. However, as said in the paragraph above, the mobility is not a constant parameter because it depends on the voltage V_{GS}, therefore, the Equation 8 is an estimate and the values obtained should be treated as such.

7 Equipment

In the following chapter detailing the equipment used to fabricate OTFTs and to measure their electrical characteristics.

7.1 Manufacturing machines

7.1.1 Dielectric deposition

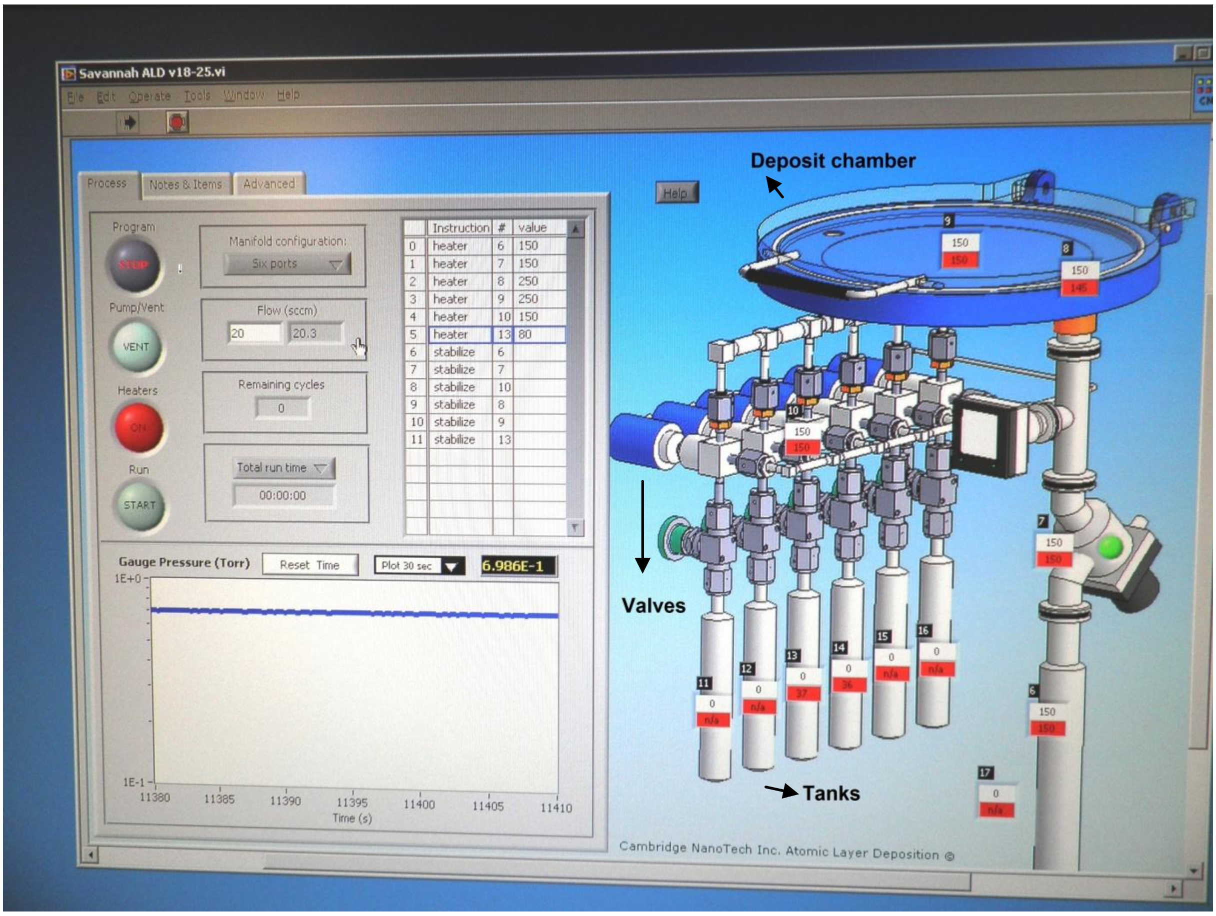
As mentioned previously, the dielectric is deposited on the substrate by atomic layer deposition (ALD) (see Figure 7.1). This technique uses gas spray on the substrate to deposit atomic layers. The enormous advantage of this technique is to be able to make deposits on surfaces that are not totally flat.

The system includes two or more source gas delivery systems with high actuation speed valves to control the length of gas pulses (see Figure 7.2), N_2 gas is used fot high speed pulse-purge cycles. The gases are introduced into a heated deposition chamber. Before to deposition, the substrate is inserted into the reactor, and is heated usually between 50-400°C. Vacuum pumping is used to control the system pressure, gas flow and insure rapid purging of the chamber after each deposition cycle [14].

This technique has, among other things, the following advantages:

- atomically flat and smooth coating
- thicknesses are determined simply by the number of cycles
- possibility to make films with large area uniformity and 3D conformality
- relatively insensitive to dust because the grows underneath dust the particles
- mixed oxides, nitrides, metals, semiconductors are possible
- possibility to work at relatively low temperatures
- low defect density

Figure 7.1. Atomic Layer Deposition machine



Manifold configuration: Six ports

Flow (sccm): 20 20.3

Remaining cycles: 0

Total run time: 00:00:00

Gauge Pressure (Torr): 6.986E-1

	Instruction	#	value
0	heater	6	150
1	heater	7	150
2	heater	8	250
3	heater	9	250
4	heater	10	150
5	heater	13	80
6	stabilize	6	
7	stabilize	7	
8	stabilize	10	
9	stabilize	8	
10	stabilize	9	
11	stabilize	13	

Figure 7.2. Deposition software interface

7.1.2 Organic materials evaporation

The evaporation process of organic materials requires precise control because the electrical characteristics of the deposit depend of this precision. The evaporation system is the UNIVEX LEYBOLD 300 model from LEYBOLD company, it consists essentially of a metal vacuum chamber that contains sensors and actuators, elements of vacuum generation and measurement equipment, control and monitoring instruments.

The vacuum chamber is cylindrical and made of stainless steel, it measures 30 cm in diameter and 40 cm high. It is in this room that the evaporation of the organic matter is made. The other elements are: a Pirani pressure sensor for pressures up to 10^{-4}mbar, a second pressure sensor (Penning type) for lower pressures, two tubes (one for P-type semiconductor and the other type N) with a heating system to evaporate semiconductors, a quartz sensor to measure deposit thickness, a shutter to start and stop the deposition process, a temperature sensor and a heating system (electrical resistance) to control the substrate temperature. These elements are defined below.

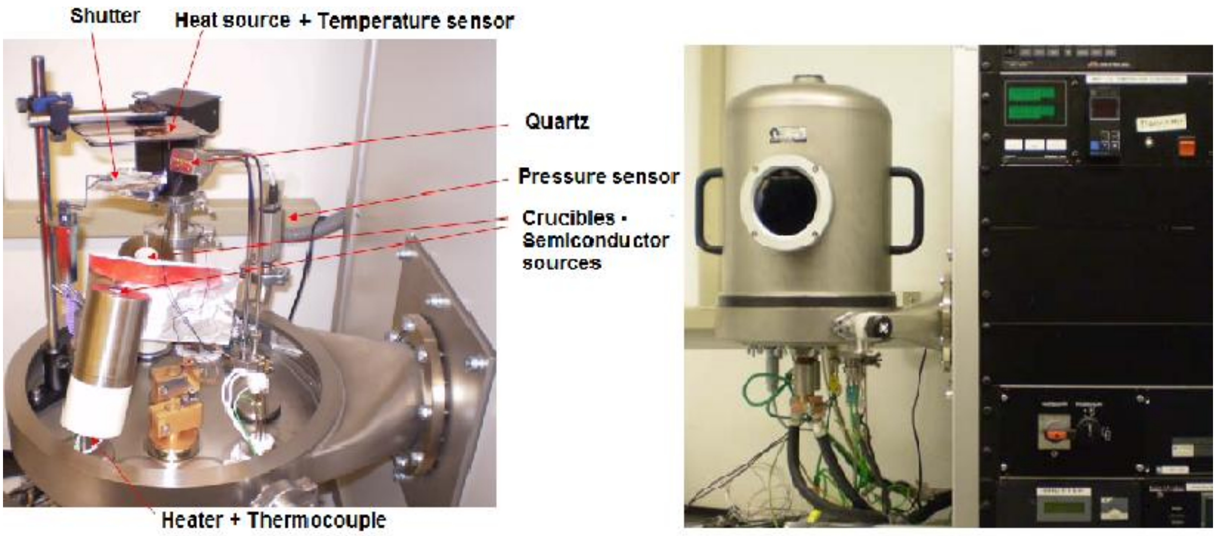


Figure 7.3. Interior and exterior views of the semiconductor evaporation system

7.1.2.1 **Pressure sensor**

The pressure is measured using two types of sensors: Pirani sensor for high pressures and Pennings sensor for lower pressures. The Pirani pressure sensor uses two filaments (often of platinum) for the two arms of a Wheatstone brigde system. There is a reference filament which is in a constant pressure while the second is in the gas being measured. The filaments are heated by a constant electric current, the resistance of the filament depends on the temperature and also on the pressure. Measuring the voltage drop across the filaments allows us to know the pressure in the chamber.

To measure very low pressure, an ionization sensor of cold cathode (also known as Penning). Using high-voltage electric shocks, emitted electrons ionize gas molecules positively and these ions are collected on a negative electrode through an electric field. The measured current at the electrode depends on the number of ions collected, which depends on the quantity of molecules in the chamber (which is a function of pressure). The sensor measures pressure from 10^{-3}mbar because at higher pressures ionized molecules tend to recombine before reaching the electrode and the measurement is not correct.

7.1.2.2 **Vacuum system**

For vacuum generation, there are two pumps connected in series, a mechanical and a turbomolecular pump.

The mechanical pump is used to create an initial vacuum from 10^{-2} to 10^{-3}mbar then turbo-molecular pump can be used safely, which can easily create a vacuum of 10^{-6}mbar inside the room. The operating mechanism of the mechanical pump is to repeat a process that is based on an expansion chamber. In our case the system uses a rotary vane pump and vanes are mounted to an eccentric rotor that rotates inside of a cavity (in our case they are 2 vanes). There are always a few vanes in contact with the pump chamber, thereby generating a continuous suction (see Figure 7.4). The speed and the number of vanes determine the vacuum pressure that can be achieved [15].

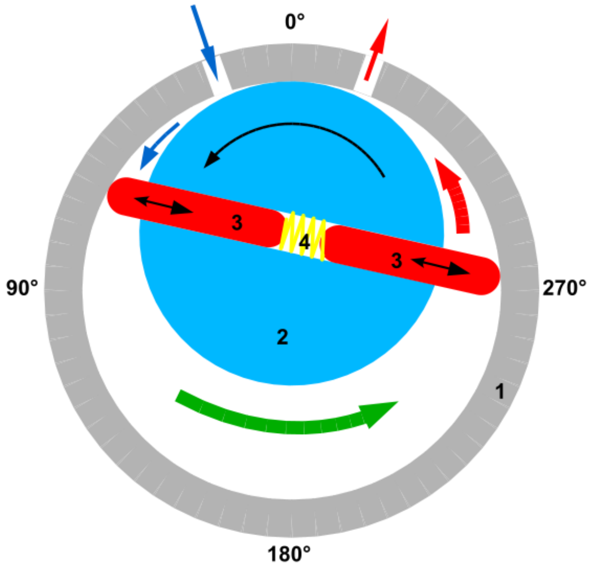


Figure 7.4. Rotary vane pump diagram. 1) pump housing 2) rotor 3) vanes 4) spring (Wikipedia, 2010)

The turbomolecular pump achieves a grater vacuum, this machine employ multiple levels of rotor and stator pairs mounted in series (see Figure 7.5). The gas captured by the upper stages is pushed into the lower stages and successively compressed to the level of the fore-vacuum (backing pump) pressure. As the gas molecules enter through the inlet, the rotor, which has a number of angled blades, hits the molecules. Thus the mechanical energy of the blades is transferred to the gas molecules. With this newly acquired momentum, the gas molecules enter into the gas transfer holes in the stator.

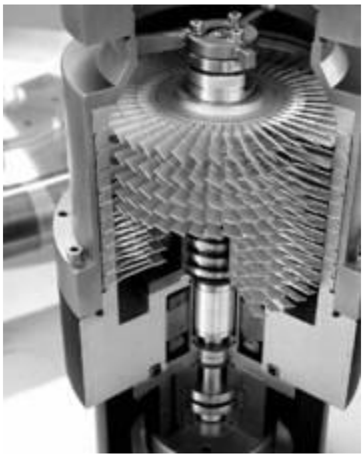


Figure 7.5. Typical turbomolecular pump

This leads them to the next stage where they again collide with the rotor surface, and this process is continued, finally leading them outwards through the exhaust [16]. When pressure is not enough low, molecules interact with each other and cause random movements. This is why we must reach a certain vacuum pump with another previously.

7.1.2.3 **Others elements of the deposition chamber**

Inside the room there are other important elements such as crucibles, the transducer of thickness and the shutter.

The crucibles are made of alumina, they are cylindrical and surrounded by a heater. In contact with the base of the crucible there is a thermocouple to measure accurately the temperature of the evaporated material. To avoid contamination, different crucibles are used for each organic material.

The quartz transducer is a circular and plane crystal and is approximately at the same height as the substrate. This quartz oscillate with a frequency inversely proportional to its thickness, so if material is added to the surface, frequency decrease and allows us to know the pace of deposit.

The shutter is a small metal plate placed horizontally between the crucible and the substrate. This shutter prevents the semiconductor deposition on the substrate, but obviously not obstructs the path to the quartz crystal. An actuator moves the shutter to a position where the semiconductor source is not obstructed; it can with this technique accurately determine the beginning and end of deposition on the substrate and thus a precise deposit can be made.

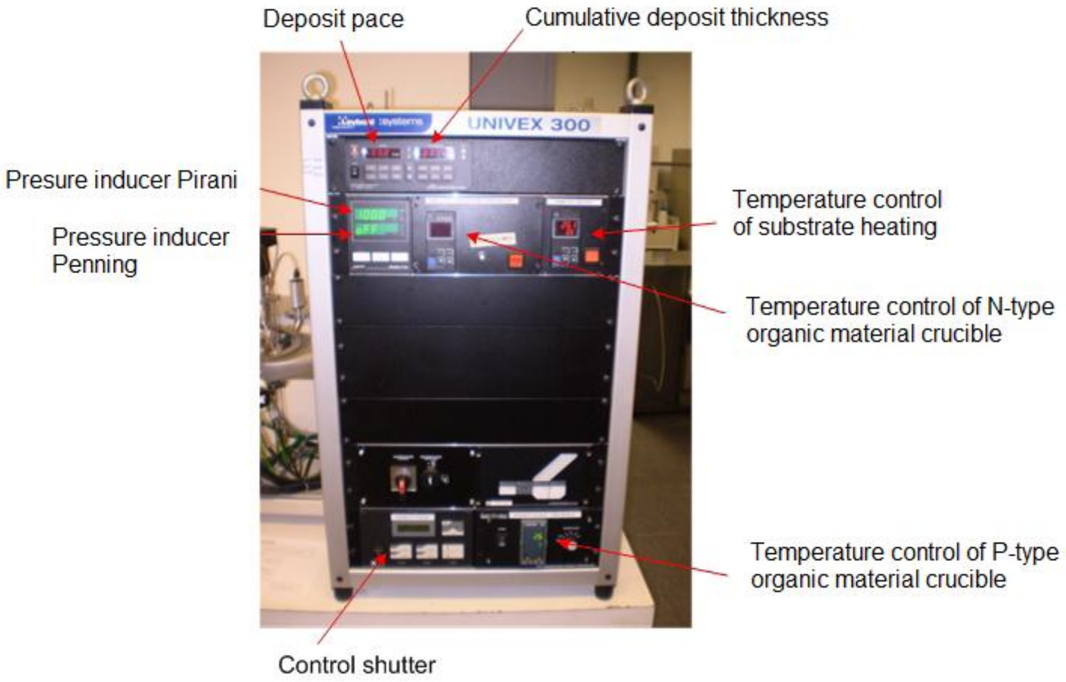


Figure 7.6. Control system of organic evaporation machine

To control the deposition there is a control panel that contains, among others, three Eurotherm PID measure the temperatures of the two crucibles and the substrate. It has a switch to open and close the shutter, a general switch can supply all the equipment, one to trigger a mechanical pump and another to activate the turbomolecular. There is also a display of pressures measured by the Pirani and Penning sensors. The deposited thickness and the rate of deposit are also shown.

7.1.3 Electrodes deposition

Evaporation and deposition of metals on a substrate (which is deposited on semiconductor layer) is not a procedure that requires special care. The parameters such as layer thickness or deposit rate don't affect hardly the device operation.

The evaporator is essentially a metal glass vacuum chamber, a mechanical vacuum pump, a turbomolecular pump, a power source and a pressure sensor. The vacuum chamber is equipped with a valve which communicates to the pumps inside the container, a small tungsten crucible containing the metal to be evaporated and support to put the substrate (Figure 7.7).

The crucible is hand cut from sheets of 50μm thick of tungsten (Figure 7.8). Its function is to close an electric circuit, which allows the current injected by a source to circulate. Since tungsten has a certain resistivity. When the current passes through the metal and produce a significant heating which is used to evaporate the desired metal on the substrate.

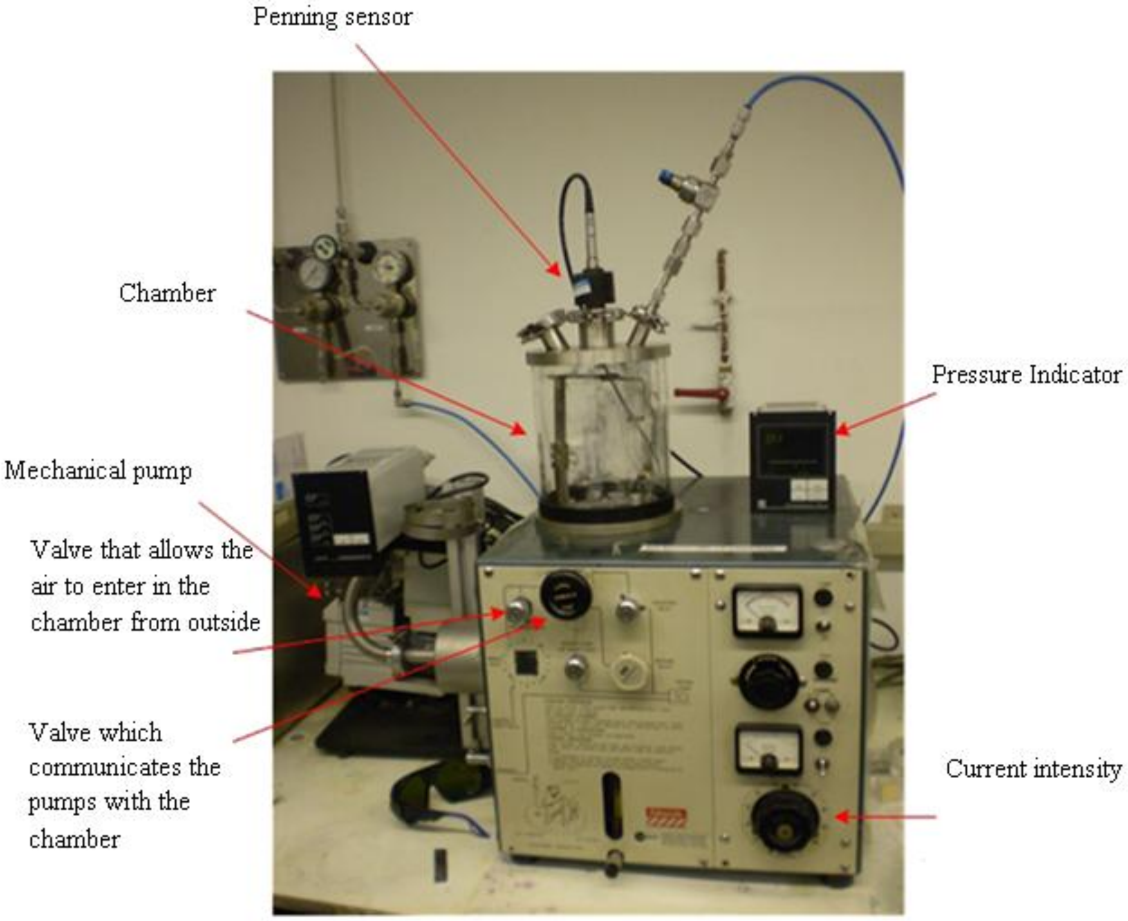


Figure 7.7. Deposit of metal electrodes

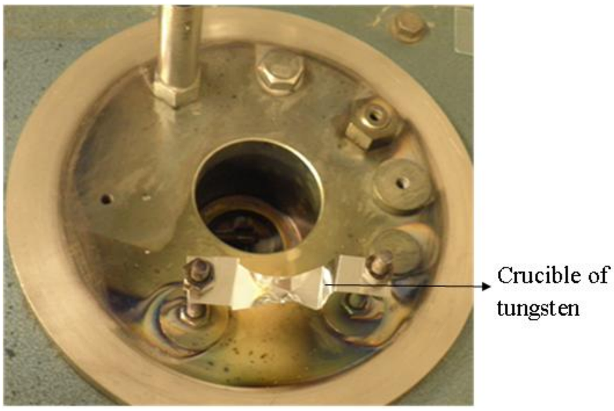


Figure 7.8. Crucible of tungsten

The chamber is cylindrical and is composed of 1 cm thick glass, 25 cm high and 20 cm in diameter. Two rubber seals to close the chamber tightly.

7.2 Measuring and tracing machine of electrical characteristics

To verify the operation of OTFT and may undergo a series of electrical measurements, they were made to the UPC. Electrical measurements were performed by the Agilent 4156C analyzer to find out the semiconductor parameters, the connection equipment is composed of a vacuum chamber, tips and cables connections. Although the analyzer can be connected to other computers, the measures have been taken with this configuration.

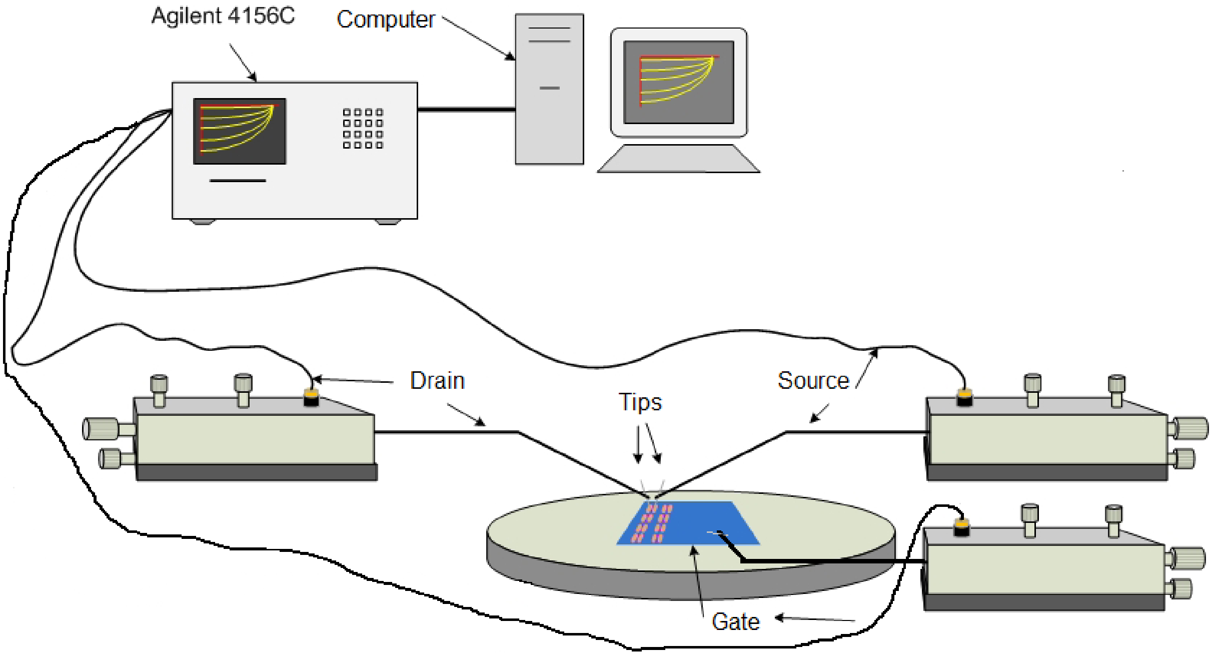


Figure 7.9. Installation of electrical characteristics measuring

The room where the substrate was placed is a cryostat but in this project all measurements were performed at room temperature, thus the heating possibilities of the machine have not been used. The room has a small glass opening just above the sample. With the aid of a microscope it is possible to connect the tips on the sample that can be moved outside the room. Thanks to a mechanical vacuum pump, it is possible to achieve a pressure under one mbar. It is necessary to avoid creating a vacuum otherwise water condense on the substrate and affect measures, longer-term vacuum also helps prevent the substrate oxidation.

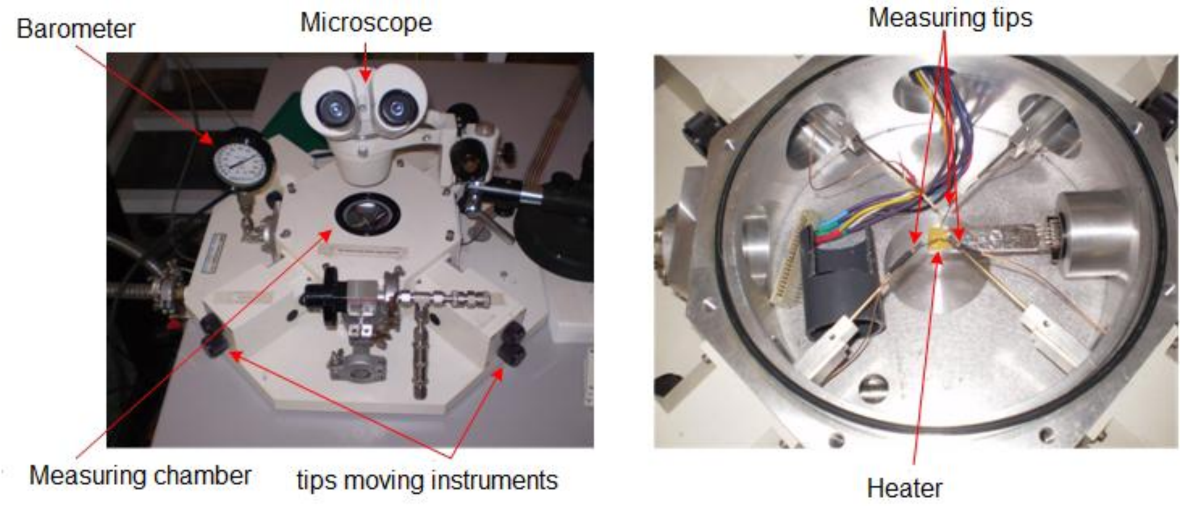


Figure 7.10. External and internal views of the cryostat

Each tip is connected by a coaxial cable to the analyzer Agilent 4156C. Under this project, we used three points to connect the drain, the source and the gate. To connect easier the gate (located under the substrate), samples are typically glued with a conductive silver paint on a conductive surface (a piece of aluminum foil for example).

8 Description of samples manufacturing

The oxide layers were deposited by atomic layer deposition in the ICFO (The Institute of Photonic Sciences), a department of UPC (Universitat Politècnica de Catalunya) in Barcelona.

The organic TFT manufacturing process was carried out in laboratories in the white room of the UPC and includes the following steps: organic material and metal electrodes deposit.

The manufacture of these devices has to be made in good conditions of cleanliness because small particles of dust can significantly affect performance. To give a magnitude of the transistor, the deposited layers have a thickness about one hundred nanometers, which is about 100 times smaller than the diameter of a hair.

8.1 Dielectric

The dielectric deposition has been made in a chamber at 150 ° C and under $4*10^{-1}$ mbar during 1 hour and 47 minutes. Each layer of Al_2O_3 is about 1.1 Å, 909 cycles were performed to reach a final layer of 100nm thick. This dielectric is deposited on the gate which is P doped with boron atoms.

8.2 Organic semiconductors deposition

First, the substrate (composed of the gate and dielectric) is placed on a plate to be attached to the structure inside the bell (vacuum chamber). For some deposits the substrate must be heated, in this case a heater and a temperature sensor are placed on the metal plate. Once the sample positioned, a mask is placed on the substrate to depose the organic material only when it is desired (see Figure 8.1), a magnet is placed on the other side of the plate to keep the mask in contact with the substrate because, as shown in **Erreur ! Source du renvoi introuvable.**, since the sample is tilted downward. The mask will be used for both, organic and metal deposition. It is very important to reduce contact with the substrate to avoid damaging it or deposit anything, the dust-free gloves and tongs are used for this purpose.

There are certain precautions to be taken to properly place the device:

- To have a good precision, it is preferable that the sample is placed at the same height as the quartz crystal
- Ensure that the shutter completely blocks the evaporation path. Evaporated molecules follow a very linear path due to the vacuum, it suffices to put the shutter on the way between the crucible and the substrate
- The crucible is slightly inclined from the vertical. If the substrate has the same inclination, the deposit is perpendicular to the substrate and the efficiency is better

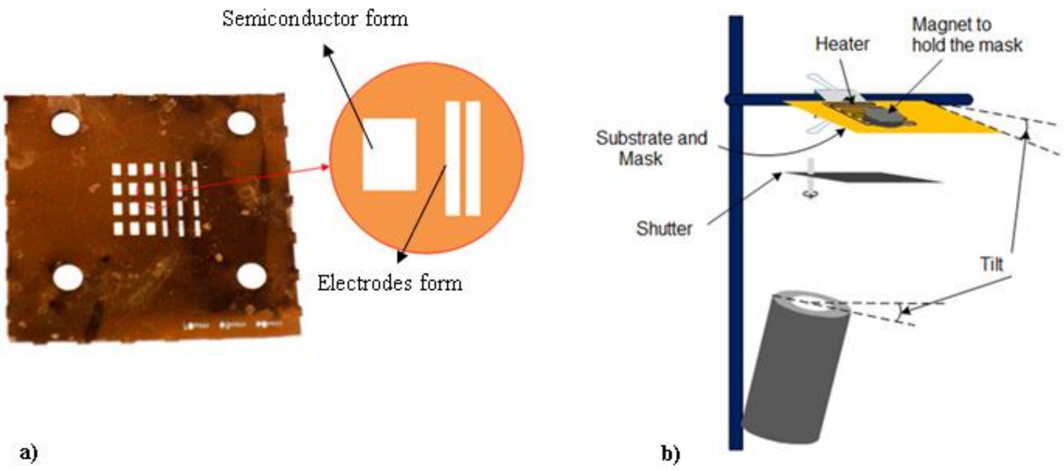


Figure 8.1. a) Mask for semiconductor and electrodes deposition b) elements arrangement in the chamber

When the sample is placed, the bell can be closed and the vacuum can be created. First, the mechanical pump is engaged, when the pressure reaches more or less than 10^{-1} mbar the turbo can be started. Evaporation cannot take place under a too high pressure, it will have to wait around two hours to reach a vacuum lower than 10-5 mbar.

A feature that promotes quality of the semiconductors layer is to deposit it with a stable and orderly pace. Sufficiently recognized by several articles [17], a low deposition rate of the material improves the molecules arrangement, what improve the electrical characteristics. The deposits were made with an approximate rate of 0.5 Å/s, what is appropriate and will form a layer in a few hours. When the correct pressure is reached, the temperature of the crucible is raised gradually to not have temperature jump. If it is necessary, the samples will be heated similarly. According to the materials, the temperature at which evaporation occurs can have very different values (approximately 150 ° C for pentacene and 250 ° C for PTCDI-C_{13}).During the evaporation, the deposit rate decreases if the temperature remains the same. To maintain a constant deposition, temperature has to be increased constantly.

The deposit is realized as the following steps:

- When the correct temperature is reached and the rate is dropped to 0.5 Å/s, the shutter is opened and the thickness indicator is set to zero

- Increase of 5 °C the crucible temperature when the rate is less than 0.4 Å/s. The goal is to maintain a rate between about 0.7 and 0.4 Å/s

- When the thickness indicator shows the desired valor (50 nm for all the semiconductors layers of this project), the shutter is closed

Finally, the heaters are reduced to zero. When the indicator of the deposition rate is nil, the pumps are stopped and the pressure rises slowly. Afterward, we have to wait a chamber pressure about 400mbars to be sure that the turbomolecular blades are stopped. At this time, the valve that communicates with the outside can be opened slowly to restore atmospheric pressure in the bell.

8.3 Electrodes deposition

Contrary to the organic material, metal evaporation is not so rigorous because the equipment used is simpler and the influence of evaporation on the overall operation of the transistor is smaller.

To avoid mixtures, each type of metal evaporated uses a different crucible. In the case of gold, a small piece of about 4 mm long and 1 mm thick is evaporated, which can thus achieve a thickness deposit of about 100 nm. The substrate is supported by a small structure to be positioned over the gold evaporation. The mask used for the organic evaporation is rotated 180 ° to position the two thin lines of the mask in front of the semiconductor filing (see Figure 8.1). A magnet is used to hold the mask against the substrate, it must be powerful enough because the high temperature affects the magnet field and the mask could fall (what would make the sample unusable).

As explained above, to do vacuum, it must first activate the mechanical pump and open the valve which communicates with the chamber. Since there is only a Penning pressure sensor and that it can be activated only from 10^{-3}mbar, the turbomolecular is turned on after waiting a few minutes. After about 5 minutes, the pressure sensor is connected and it takes a vacuum of about 5.10^{-5} mbar to evaporate gold, waiting two hours is generally sufficient.

The evaporation is performed by passing an electric current in the crucible. In this project the crucible is tungsten because it can be raised to high temperature without his melting. It should slowly turn the current intensity switch until the metal evaporation (80 amps for gold, used in this project). It is possible to see that the metal melts and shrinks until it disappears. It is important not to apply a high intensity for too long (not more than 15 seconds) because it could damage the chamber and its components.

When evaporation is completely finished, the turbomolecular and the pressure sensor are turned off. This evaporator has a valve between the chamber and pumps, which can stop the pump and allow us to open the room. For added security, this valve is kept closed for a few minutes until the turbo is stopped. After that, the mechanical pump can be stopped and the chamber valve can be opened.

Finally, below, a picture (done with an optical microscope) of one of the OTFTs analyzed in this final thesis. It is very easy to see the organic semiconductor deposit and the gold electrodes.

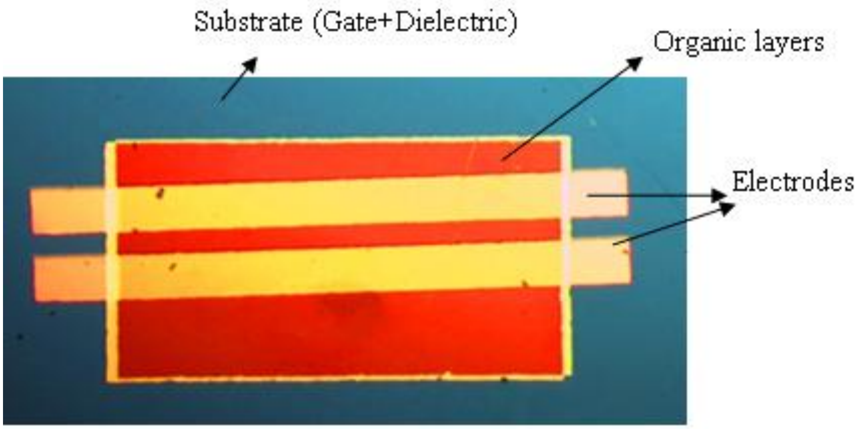


Figure 8.2. Photo of an OTFT made by the method described in Chapter 8, by an optical microscope

9 Samples analysis

9.1 Physical characteristics

Summary of the samples physical characteristics :

Thicknesses :

- Gate (c-Silicium): 300 µm
- Dielectric (Al_2O_3) : 100 nm
- Semiconductor (PTCDI-C_{13} and pentacene) : 50 nm
- Drain and Source (gold) : +/- 100 nm

Deposit conditions :

- Dielectric (Al_2O_3) :
    - Pressure ≈ 4.10^{-1} mbar
    - Temperature ≈ 150°C
- Semiconductors :
    - Pentacene :
        - Pressure ≈ 10^{-5} mbar
        - Temperature ≈ 150°C
    - PTCDI-C_{13} :
        - Pressure ≈ 10^{-5} mbar
        - Temperature ≈ 250°C
- Electrodes (gold)
    - Pressure ≈ 5.10^{-5} mbars

Other characteristics :

- Width : W = 1915 µm
- Length : L = 90 µm
- $\varepsilon_{ox}(Al_2O_3) = 7.5$ F.m^{-1}
- $C_{ox} = 6.6375\ 10^{-8}$ F.cm^2

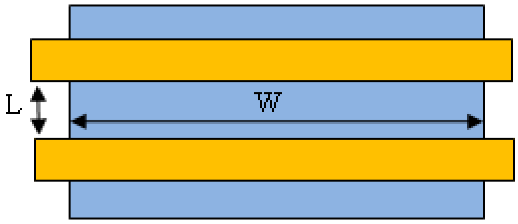


Figure 9.1. Representation of width and length

9.1.1 P-type pentacene structure

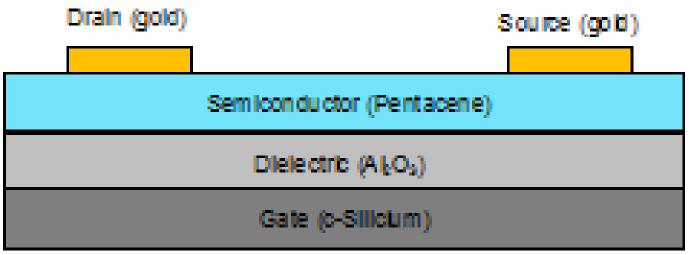


Figure 9.2. P-type pentacene structure

9.1.2 N-type PTCDI-C13 structure

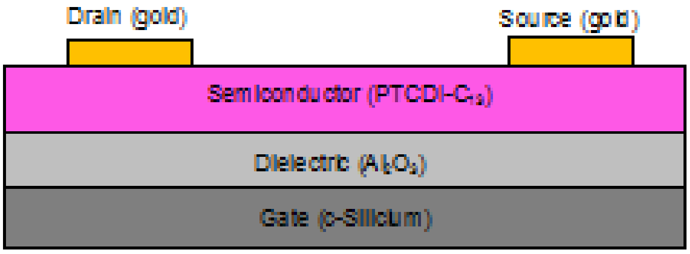


Figure 9.3. N-type PTCDI-C_{13} structure

9.1.3 Pentacene and PTCDI-C_{13} structure

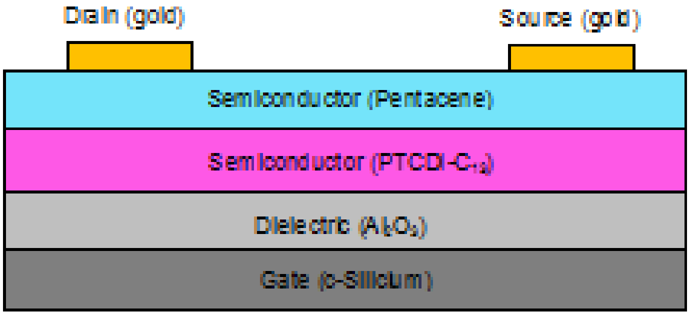


Figure 9.4. Pentacene and PTCDI-C_{13} structure

9.1.4 PTCDI-C_{13} and pentacene structure

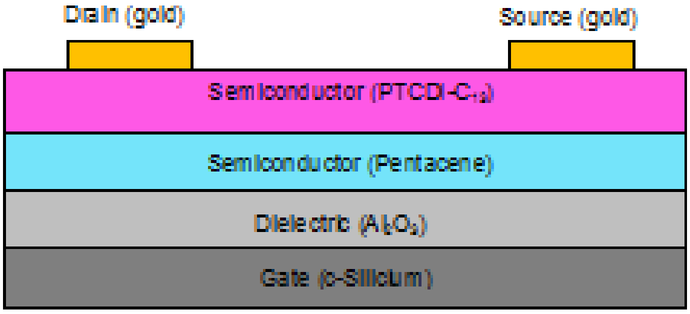


Figure 9.5. PTCDI-C_{13} and pentacene structure

9.2 Electrical characteristics without light

All these following electrical measures were made without light. For comparisons with literature results, it has to always take into consideration the sample characteristics. Thus, for example to compare currents of the output characteristics, the ration W/L influences the amount of current (see Equation 1 in chapter 6).

9.2.1 P-type pentacene

9.2.1.1 Output characteristic

Pentacene as P-type, the gate voltage has to be negative to create a channel between drain and source and consequently, a hole current (see Chapter 6). The current is negative because it is defined positive from the drain to the source since the source is the electrical ground, the drain-source voltage is negative too.

The graph shows an output characteristic as typical crystalline silicon MOSFET. Indeed, the current is almost linear for small V_{DS} voltages and saturates for higher V_{DS} voltages (in absolute values). This assessment is very important to affirm that the OTFT operate properly and that the result is not simply a measure of resistance between two electrodes.

Submitted to lower voltage than -15 V (approximately), the transistor conducts significant current. As comparison, an OTFT using pentacene as semiconductor and studied in a Korean article [20], has an I_{DS} around 8.10^{-7} A, for the same OTFT structure but using SiO_2 as insulator. As mentioned above, It should be noted that the current depends on the ratio W/L (see Equation 1 in Chapter 6), which is almost 10 times greater in this article.

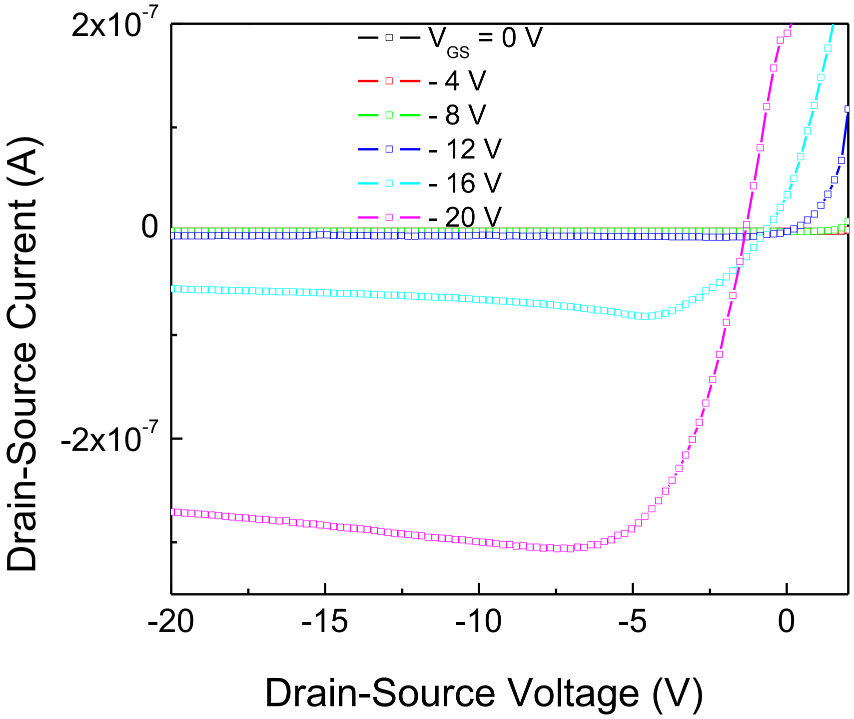


Figure 9.6. Output characteristic of the OTFT with P-type semiconductor (pentacene)

9.2.1.2 Transfer characteristic

As we know, an observation that can be done from the transfer is to see the current behavior between drain and source when moving from a state of non-conductive (off) to a state of conduction (on). TFTs are usually used as switches, it is important to measure the quality of the device, i.e. the current when V_{GS}=0V and when $|V_{GS}|>|V_t|$. This sample shows an I_{on}/I_{off} current ratio of about 10^4 from V_{GS}= -20V to V_{GS}=0V, what is quite good. It shows the degree of accumulation of holes along the channel. Some observations can be done:

- From V_{GS} = - 5V V_{GS} = V_t: there is an exponential growth of current, due to the massive accumulation of holes in the channel. The current is still too low to consider that the device conduce current

- From V_{GS} = V_t to V_{GS} = - 14V: in this area there is a slowdown in the rise of I_{DS}, which shows that the device enter in the saturation area. This area marks the transition between exponential and linear growth. In general, the top limit of this area is called V_{on} because it is from this point that there is less growth of current

- When V_{GS} < - 14V: this part of the graph is almost linear, the holes accumulation in the channel slowed sharply. It is considered that from the beginning of this zone, the device behaves as a resistor with a V_{GS} tension to its terminals

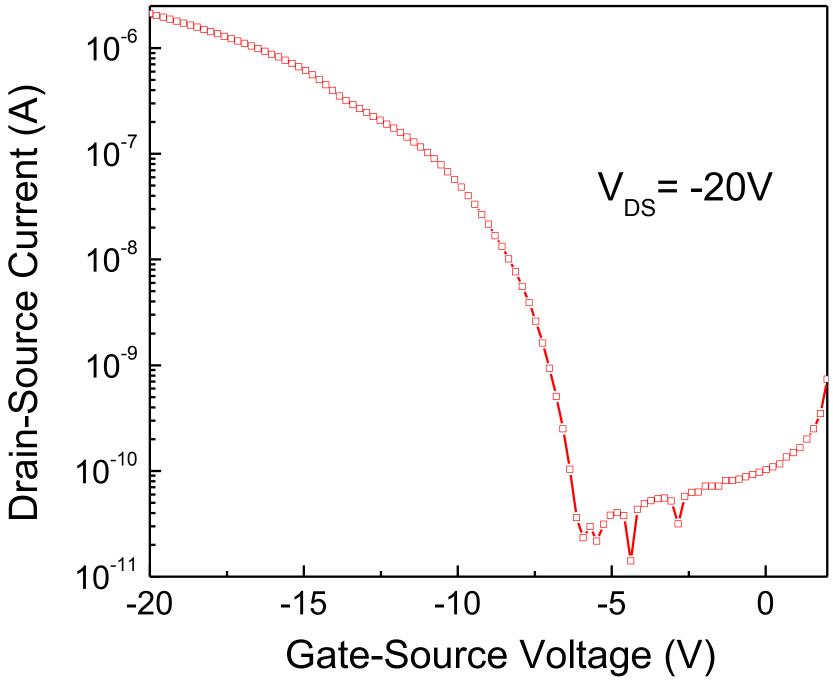


Figure 9.7. Transfer characteristic of the OTFT with P-type semiconductor (pentacene)

9.2.1.3 Saturation characteristic

The graph of saturation used to calculate the charge carrier mobility and threshold voltage in a simple manner and with a good approximation. From this graph, a hole mobility μ=0.05 $cm^2/V.s$ and a threshold voltage V_t= - 10.26 V are found.

The mobility is rather low, this may be due to some problems during the pentacene deposition but the results are still comparable to some scientific results. The threshold voltage is quite low, what is good.

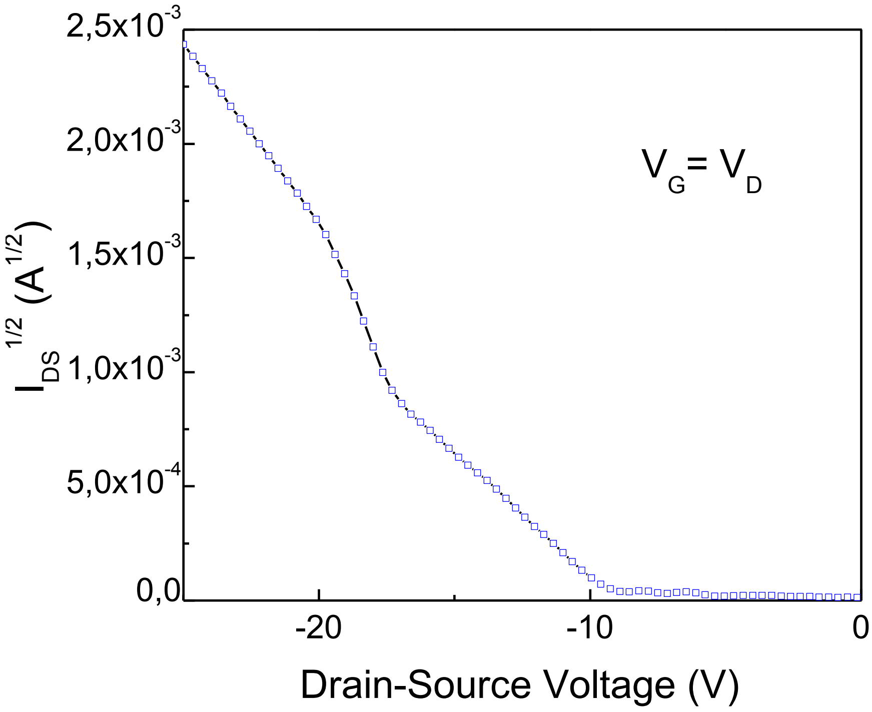


Figure 9.8. Saturation characteristic of the OTFT with P-type semiconductor (pentacene)

9.2.2 N-type PTCDI-C_{13}

9.2.2.1 Output characteristic

It is easy to observe that under a gate tension of 35 volts there is almost no current flowing between the drain and the source. By cons, for higher V_{GS} values the current can easily reach some μA, with a resistive zone and a zone of saturation well defined. In comparison to what exists in the literature [21], these results are really significant.

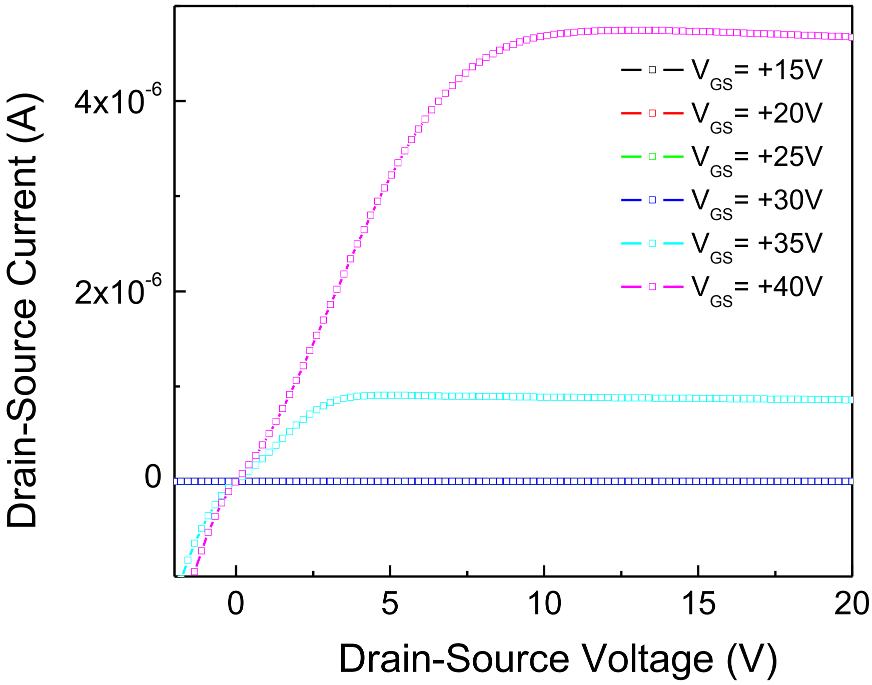


Figure 9.9. Output characteristic of the OTFT with P-type semiconductor (PTCDI-C_{13})

9.2.2.2 Transfer characteristic

The behavior of the OTFT transfer characteristic is not unusual since it has an I_{on}/I_{off} current ratio of about 10^2 (between V_{GS} = 0V V_{GS} = + 40V and), which is relatively low. The same division in three zones can be made in this graph, as for the pentacene, with the difference that it accumulates electrons and that the gate voltage is opposite in sign.

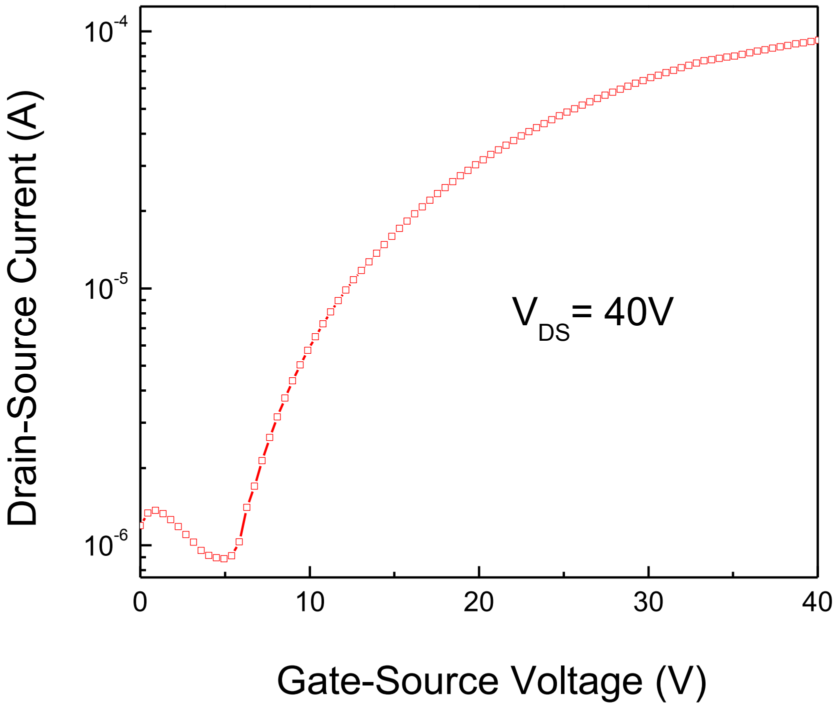


Figure 9.10. Transfer characteristic of the OTFT with P-type semiconductor (PTCDI-C_{13})

9.2.2.3 Saturation characteristic

As mentioned earlier, this graph determines the charge carrier mobility (electrons in this case) which is 0.16 cm^2/V.s, and a threshold voltage of 22.9 V.

The mobility is rather high and is comparable to those found in the articles [21]. By cons, the threshold voltage is too high to commercialize this technology like this, but it corresponds to the results obtained by some other researchers.

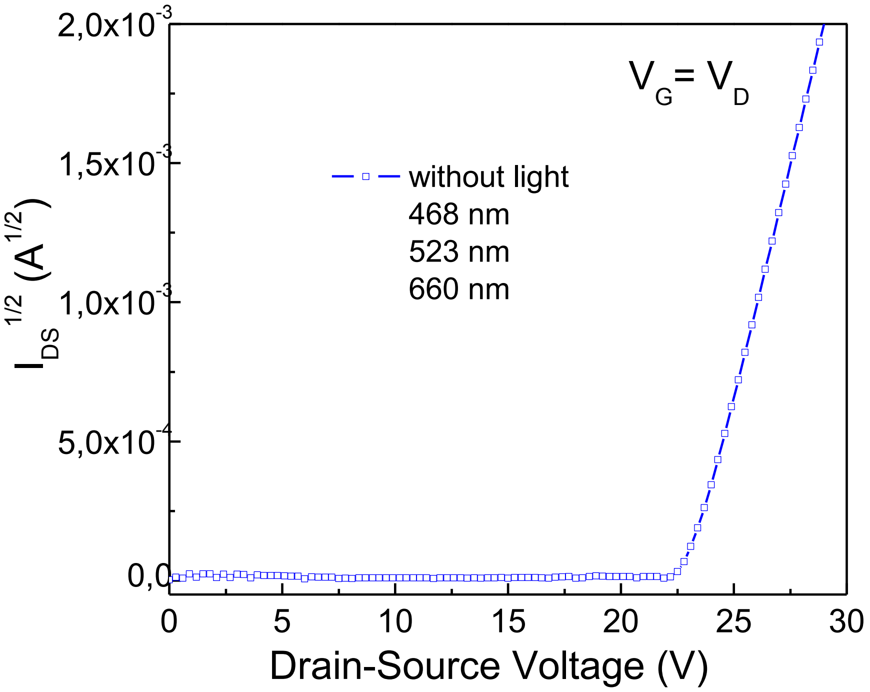


Figure 9.11. Saturation characteristic of the OTFT with P-type semiconductor (PTCDI-C_{13})

9.2.3 Pentacene and PTCDI-C13

9.2.3.1 Output characteristic

It can be observed that this OTFT is ambipolar. The current reaches a few microamperes, for holes and electrons currents.

Indeed, for gate and drain voltages both negative (as in the case of a P-type transistor), the transistor conducts holes. On the contrary, when the gate and drain voltages are both positive (as in the case of an N-type transistor), the transistor conducts electrons. In both cases, the ohmic and saturation regions are clearly present.

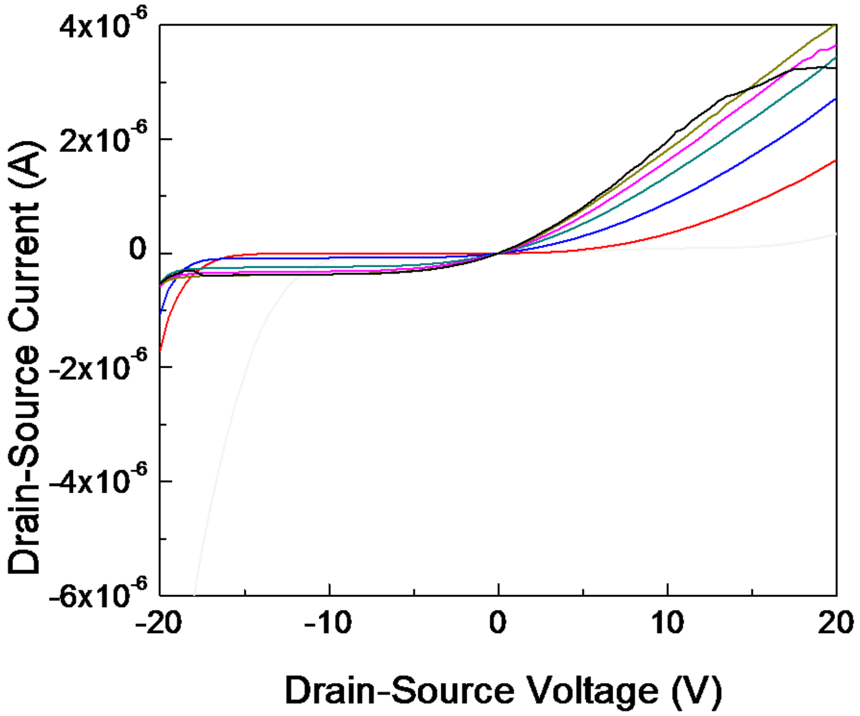


Figure 9.12. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13})

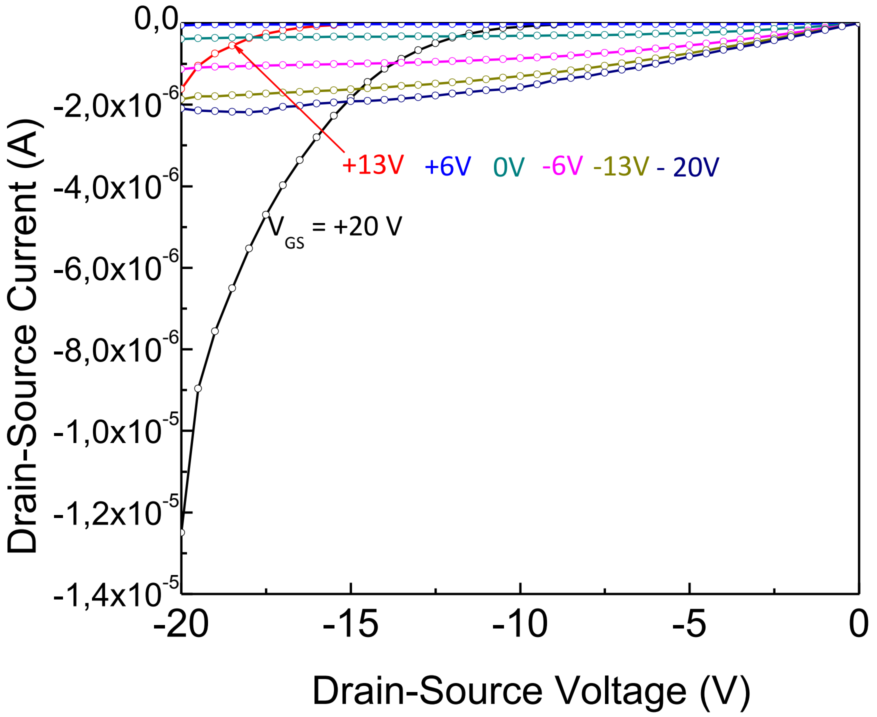


Figure 9.13. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), negative part

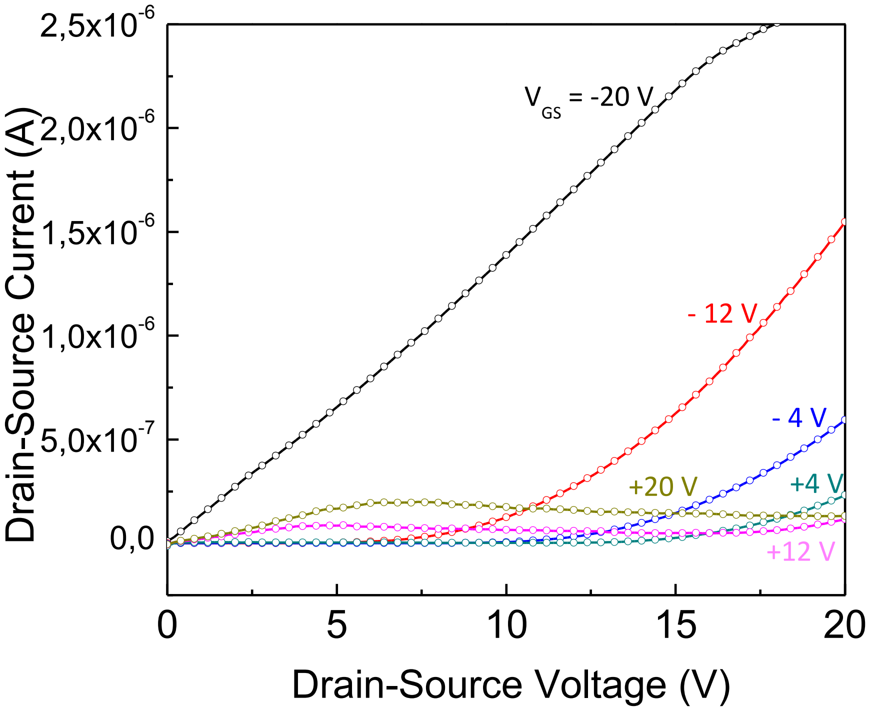


Figure 9.14. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), positive part

9.2.3.2 Transfer characteristic

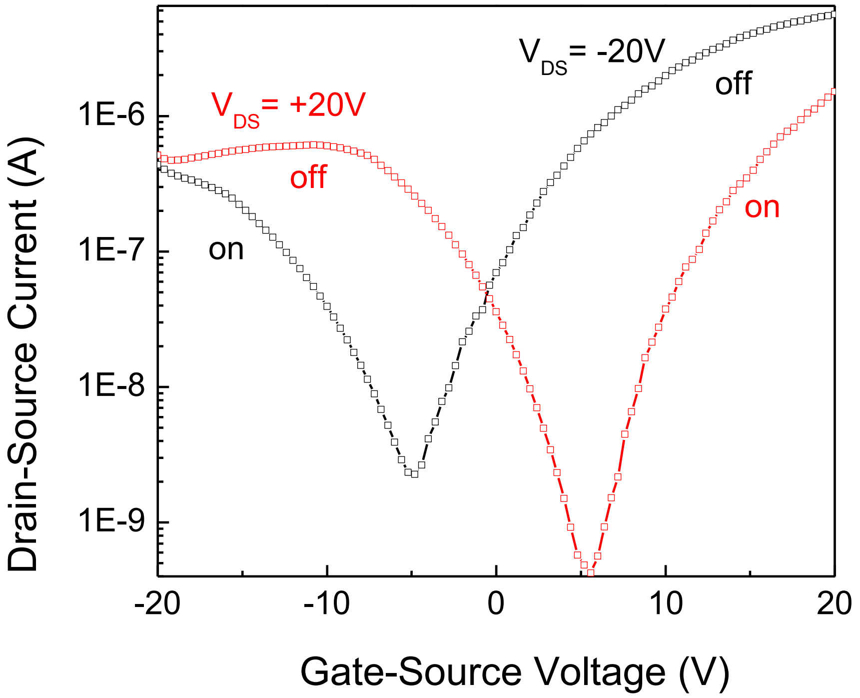


Figure 9.15. Transfer characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), V_{DS}= + 20V and V_{DS}= - 20V

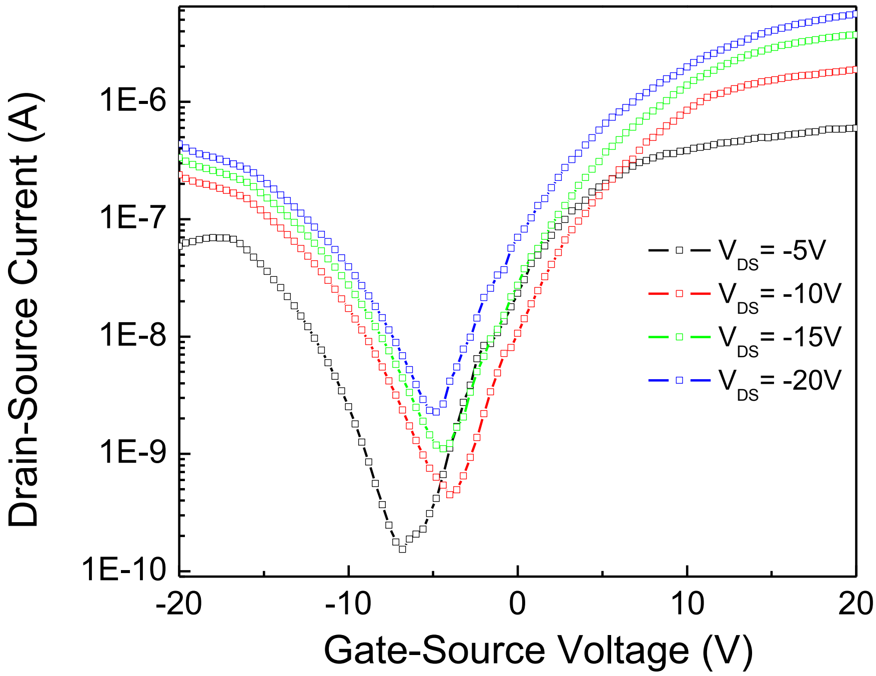


Figure 9.16. Transfer characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), VDS= - 5V, - 10V, - 15V, - 20V

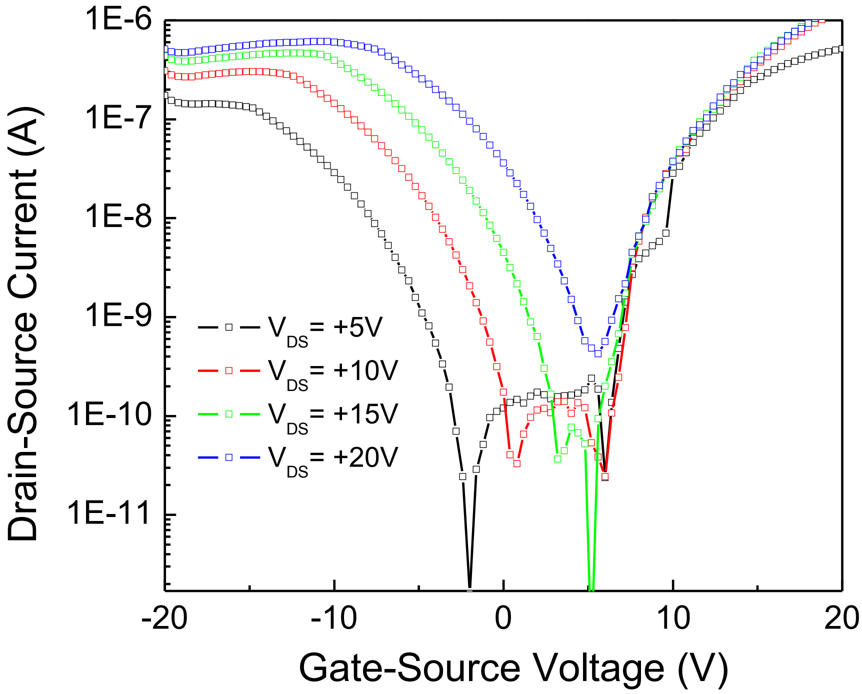


Figure 9.172. Transfer characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), VDS= +5V, +10V, +15V, +20V

9.2.3.3 **Saturation characteristic**

This graph shows very clearly that this OTFT is able to lead holes when the drain voltage is negative and to lead electrons when the drain voltage is positive. The holes and electrons mobilities are respectively 0.004 cm^2/V.s and 0.045 cm^2/V.s. The threshold voltages of the holes and electrons conductions are respectively -4.5 V and 6.8 V, which is good because they are quite low.

A previous study has been made on the same type of devices using pentacene and PTCDI-C$_{13}$ as semiconductors and PMMA[5] as insulator [22]. Their mobilities are comparable to those of this sample. It should be noted that the charges mobilities of the ambipolar transistors are always lower than those of simple transistors.

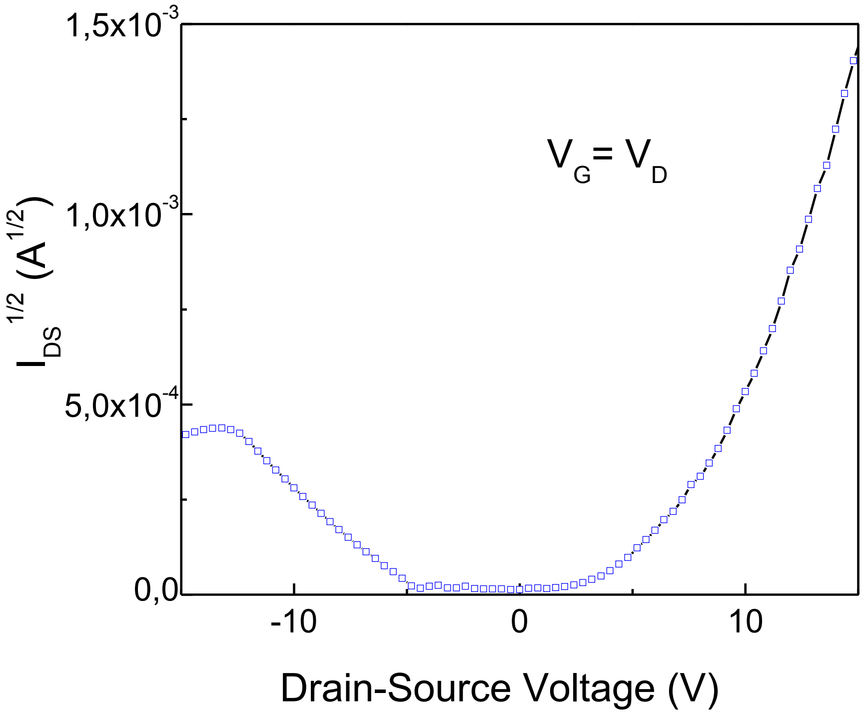


Figure 9.18. Saturation characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C$_{13}$)

---

[5] Poly(methyl methacrylate)

9.2.4 PTCDI-C_{13} and pentacene

9.2.4.1 Output characteristic

As the previous sample, it can be observed that this OTFT is ambipolar. The current reaches a few microamperes, for holes current and for the electrons current, but the gate voltage has to be higher than the other ambipolar OTFT.

Indeed, for gate and drain voltages both negative (as in the case of a P-type transistor), the transistor conducts holes. On the contrary, when the gate and drain voltages are both positive (as in the case of an N-type transistor), the transistor conducts electrons. In both cases, the ohmic and saturation regions are clearly present.

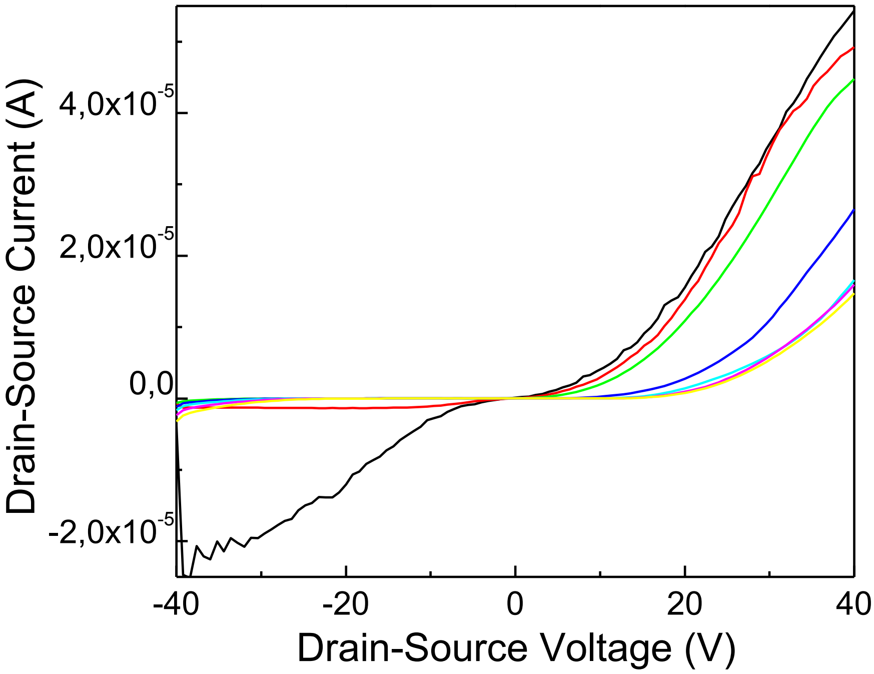


Figure 9.19. Output characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene)

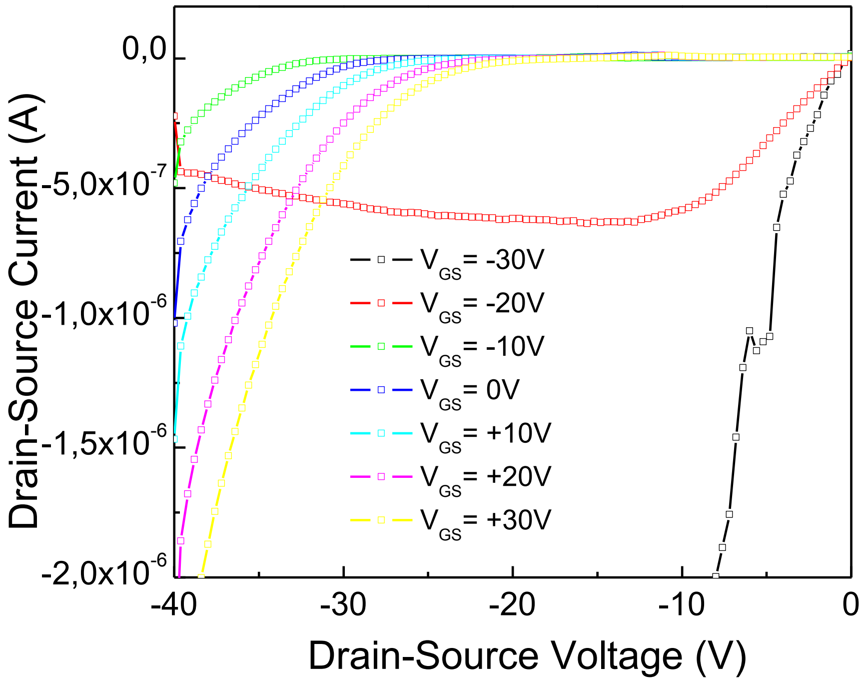


Figure 9.20. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C$_{13}$), negative part

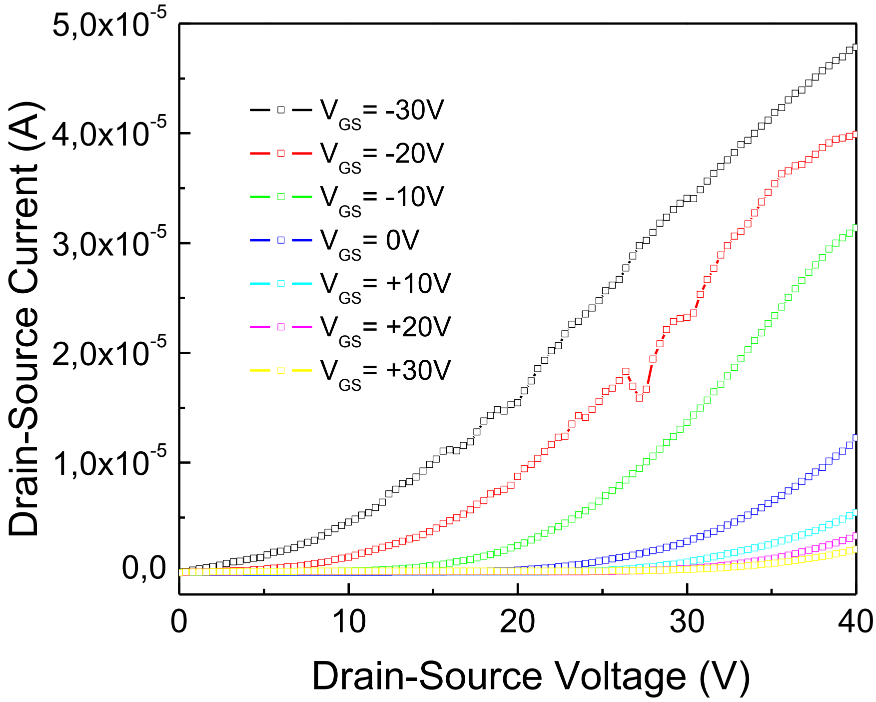


Figure 9.21. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C$_{13}$), positive part

To see better the electrons current, here is a zoom of the Figure 2.1:

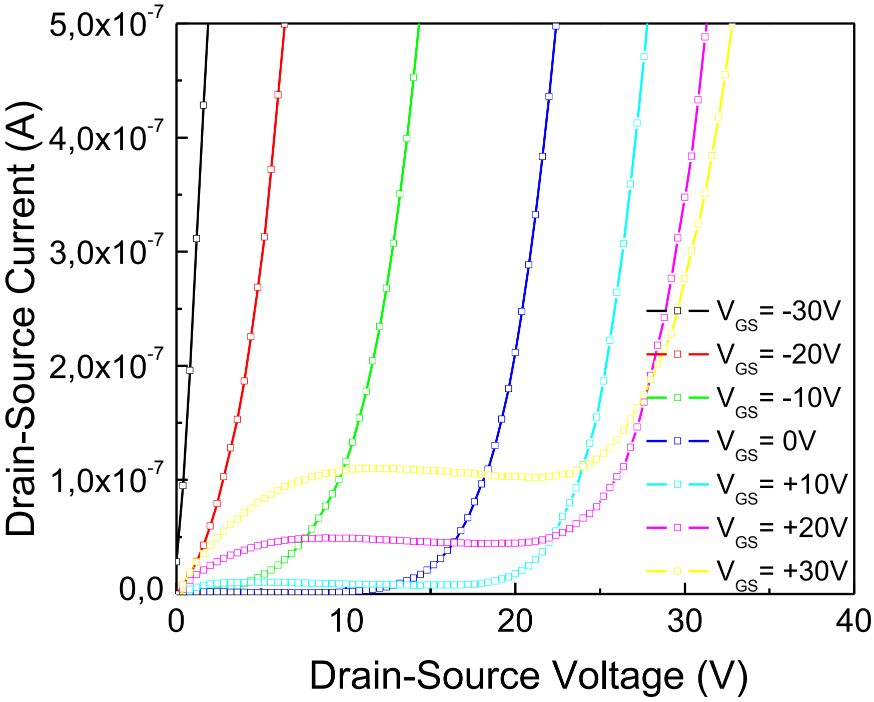


Figure 9.22. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C13), positive part, zoom

9.2.4.2 Transfer characteristic

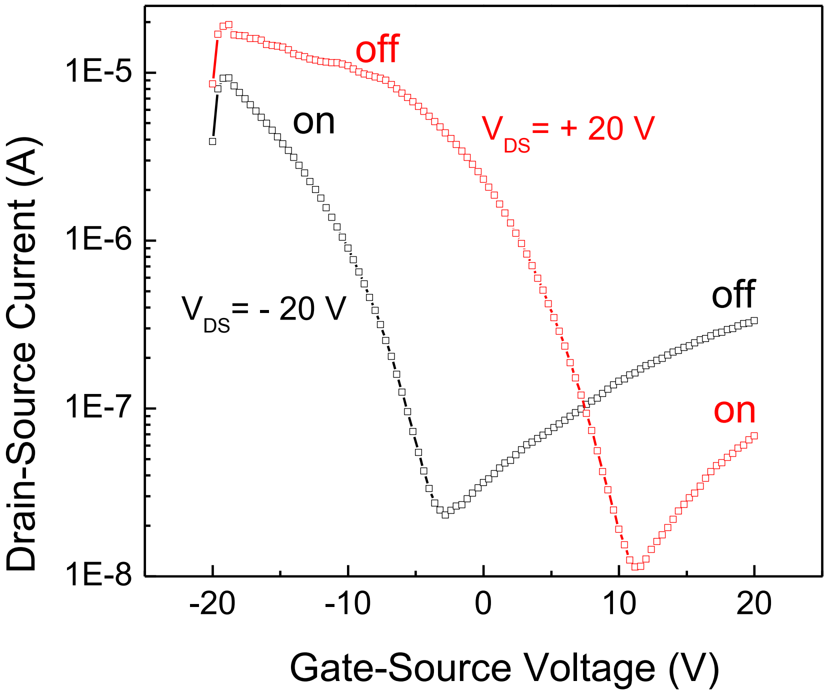


Figure 9.23. Transfer characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), V_{DS}= + 20V and V_{DS}= - 20V

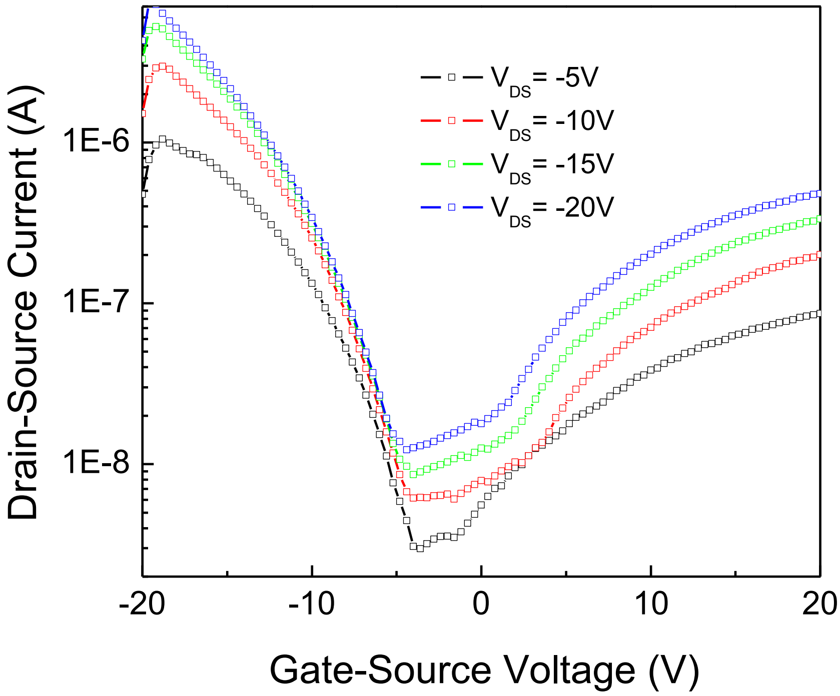


Figure 9.24. Transfer characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), VDS= - 5V, - 10V, - 15V, - 20V

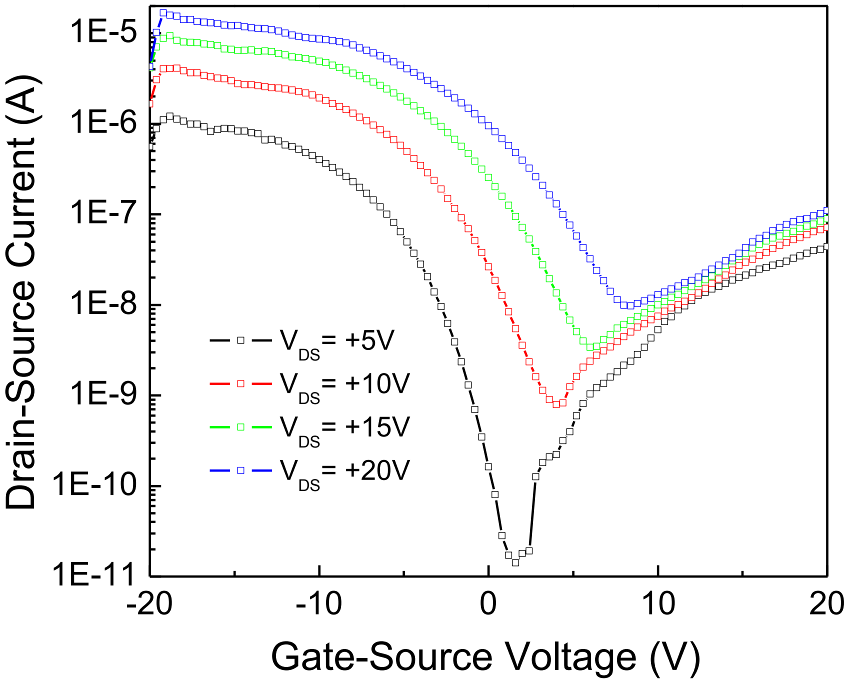


Figure 9.25. Transfer characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C13 and pentacene), VDS= +5V, +10V, +15V, +20V

9.2.4.3 Saturation characteristic

This graph shows very clearly that this OTFT is able to lead holes when the drain voltage is negative and to lead electrons when the drain voltage is positive. The holes and electrons mobilities are respectively 0.023 $cm^2/V.s$ and 0.016 $cm^2/V.s$. The threshold voltages of the holes and electrons conductions are respectively -0.45 V and 8.12 V, which is good because it is quite low.

As the previous sample, the mobilities are comparable to what exists already in the scientific papers. Compared to the previous sample, the holes mobility is slightly lower and the electrons mobility is significantly higher.

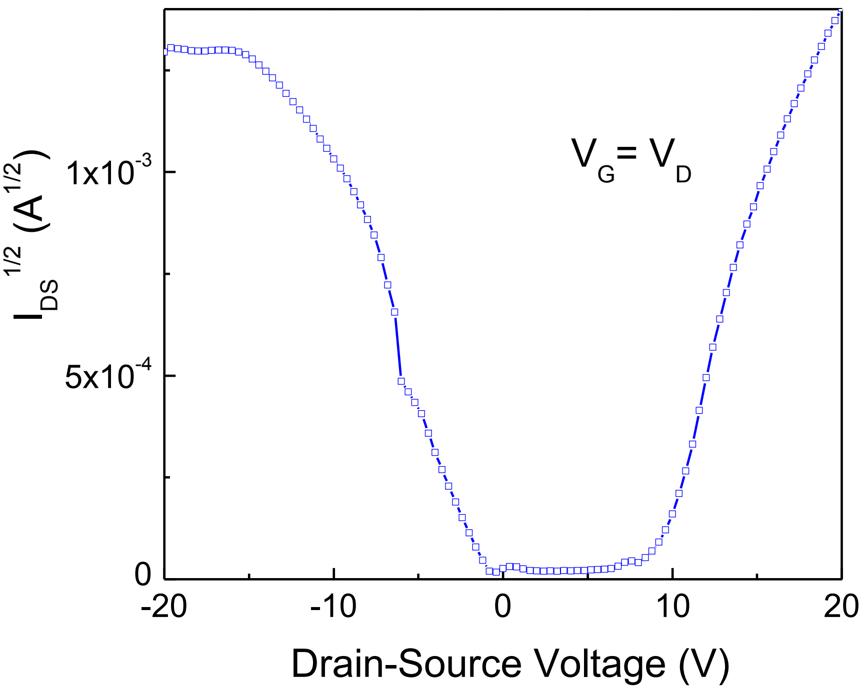


Figure 9.26. Saturation characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene)

9.3 Results summary

Regarding the thin-film samples of pentacene and PTCDI-C_{13} alone the results are those expected. Indeed, the results of these two samples are comparable to what exists in the literature, with the advantage that all the manufacture steps have been made at low temperature.

Concerning the two samples with heterostructure of pentacene and PTCDI-C_{13}, the results are really very encouraging. Indeed, they have good electrical characteristics in comparison to what has already been achieved with organic materials. The innovation of these devices is that the samples were performed at low temperature (to recall, the insulator of Al_2O_3 was deposited at 150°C). This sort of devices is very interesting because is able to conduce holes and electrons, what offers inter alia the possibility to fabricate CMOS inverter using the same transistors while this sort of inverter requires usually one P-type and one N-type transistors.

The difference in electrical characteristics between the two ambipolar OTFTs shows us that the device structure has a significant influence since in this case the two semiconductors have simply reversed. Thus, even better electrical characteristics can certainly be found.

10 Photovoltaic approach

10.1 Illumination technique

As explained in the introduction, the various OTFTs were subjected to illuminations with different wavelengths to understand better the absorption influence of the different semiconductor layers on the electrical characteristics.

Different LEDs have been selected for this illumination

1) Manufacturer: Kingbright
   Manufacturer reference: L-7104QBC-D
   Wavelength of emitted light: 468 nm
   Light intensity: 1500 mcd (millicandela)

2) Manufacturer: OSRAM Opto Semiconductors
   Manufacturer reference: LT 3333-UV
   Wavelength of emitted light: 523 nm
   Light intensity: 1120 mcd (millicandela)

3) Manufacturer: Ledtech
   Manufacturer reference: L07R3000G3
   Wavelength of emitted light: 660 nm
   Light intensity: 600 mcd (millicandela)

These wavelengths were chosen according the absorption graph of the two organic semiconductors [18]. Indeed, pentacene and PTCDI-C_{13} absorb strongly light having, respectively, a wavelength of about 660nm and 480nm (see **Erreur ! Source du renvoi introuvable.**). A third wavelength situated between the two previous has been chosen for further understanding.

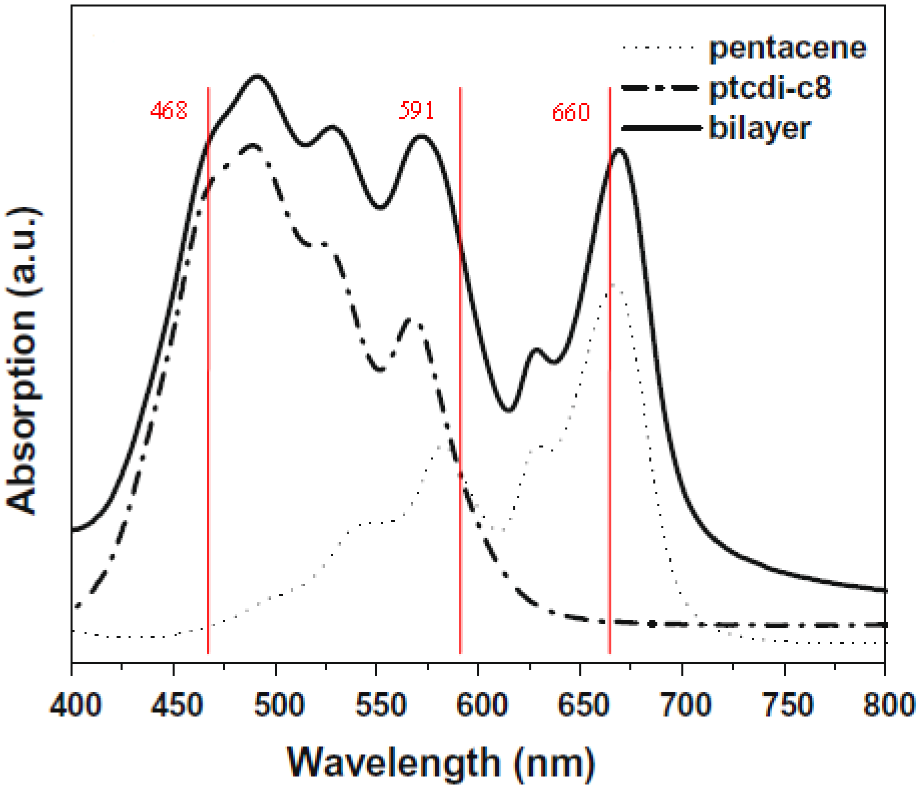


Figure 10.1. Absorption spectrum of a 50 nm thick pentacene film, 40 nm thick PTCDI-C8 film and the pentacene/PTCDI-C8 heterojunctions deposited on glass substrates (Karak, 2009)

10.2 Electrical characteristics with illumination

10.2.1 P-type pentacene

10.2.1.1 Output characteristic

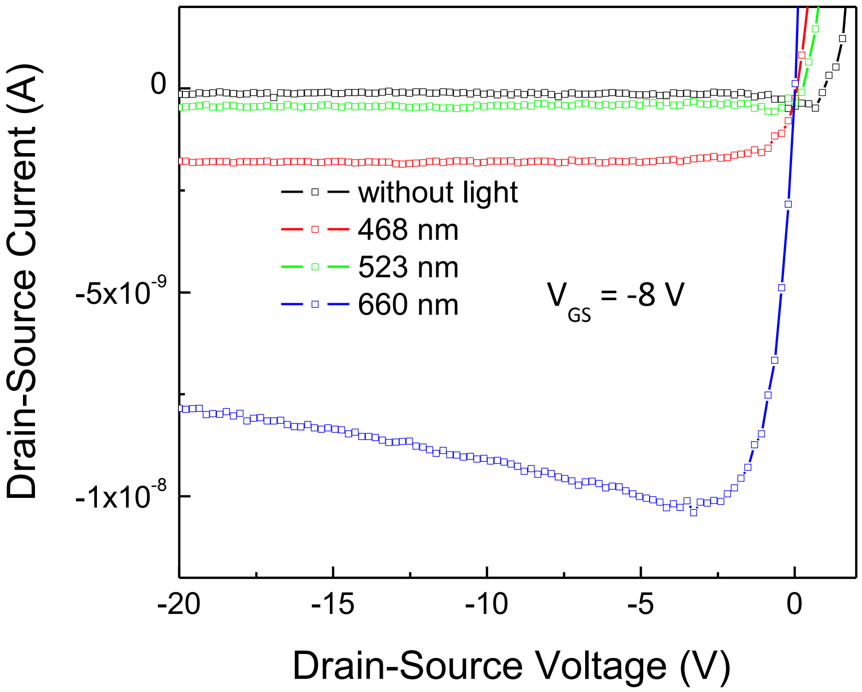


Figure 10.2. Output characteristic of the P-type (pentacene) OTFT with several illuminations and V_{GS}= - 8V

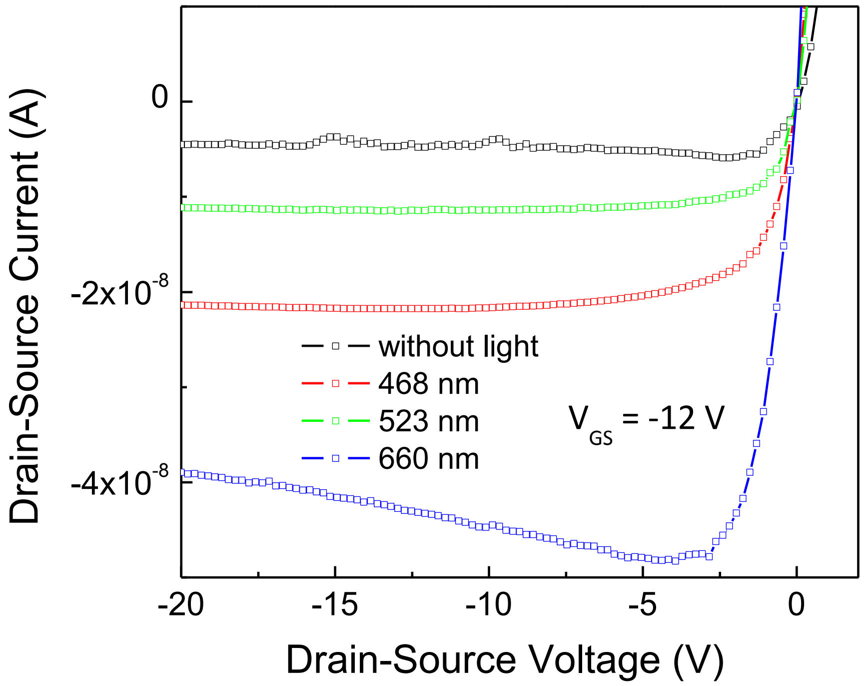


Figure 10.3. Output characteristic of the P-type (pentacene) OTFT with several illuminations and V_{GS}= -12V

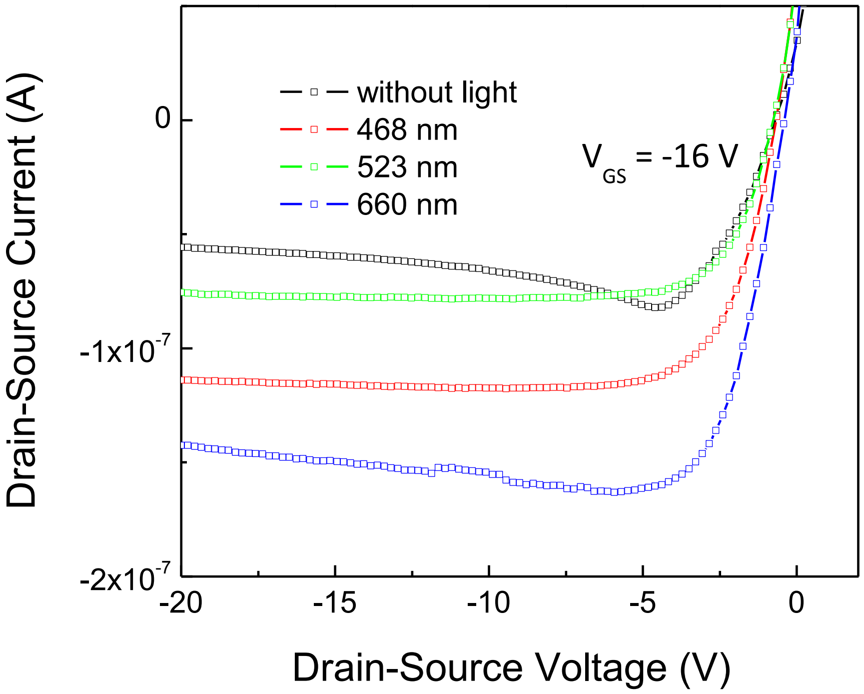


Figure 10.4. Output characteristic of the P-type (pentacene) OTFT with several illuminations and V_{GS}= - 16V

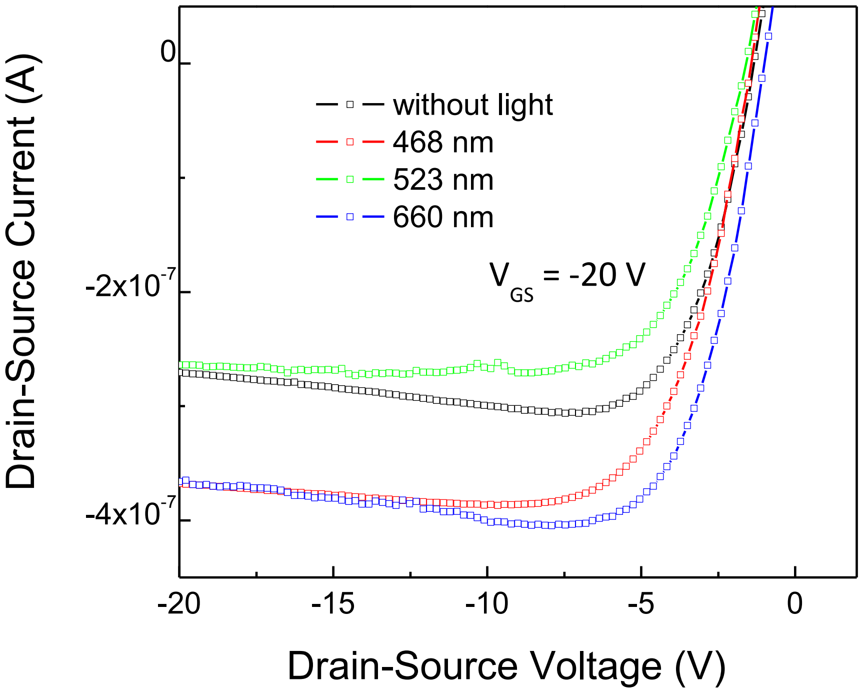


Figure 10.5. Output characteristic of the P-type (pentacene) OTFT with several illuminations and V_{GS}= - 20V

10.2.1.2 Transfer characteristic

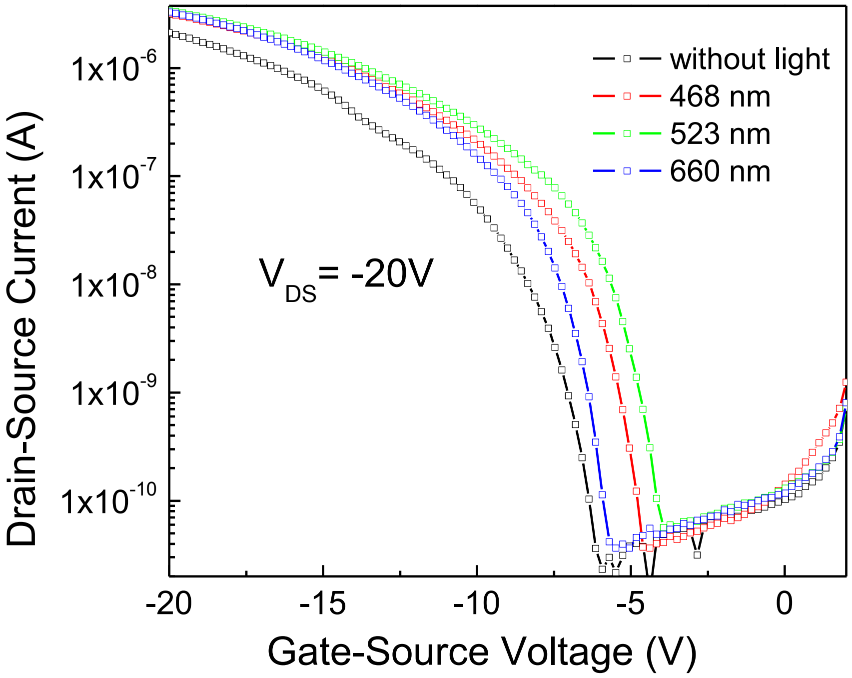


Figure 10.6. Transfer characteristic of the P-type (pentacene) OTFT with several illuminations and V_{DS}= - 20V

10.2.1.3 **Saturation characteristic**

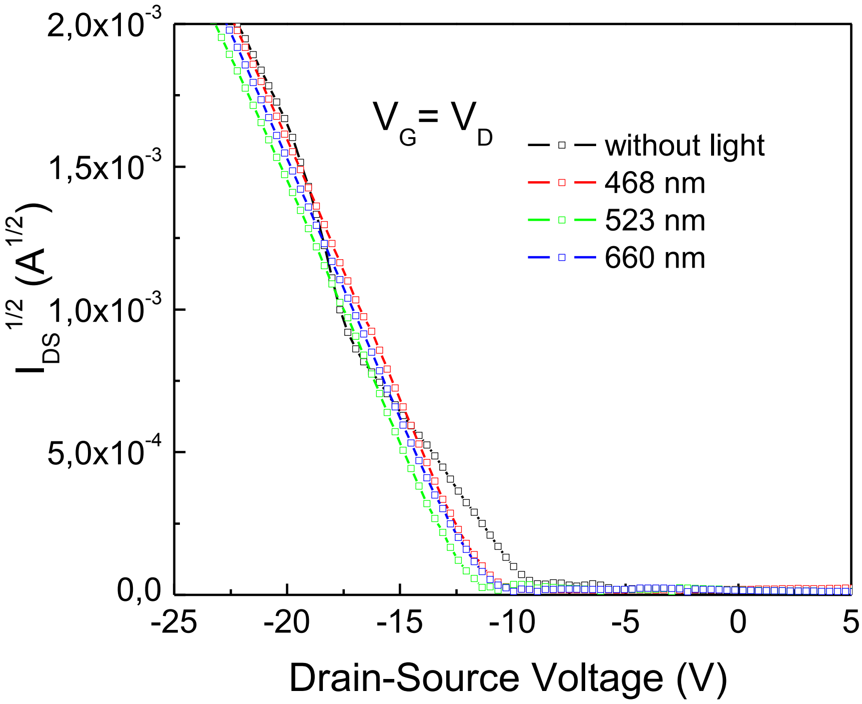


Figure 10.7. Saturation characteristic of the P-type (pentacene) OTFT with several illuminations and V_G=V_D

10.2.2 N-type PTCDI-C_{13}

10.2.2.1 Output characteristic

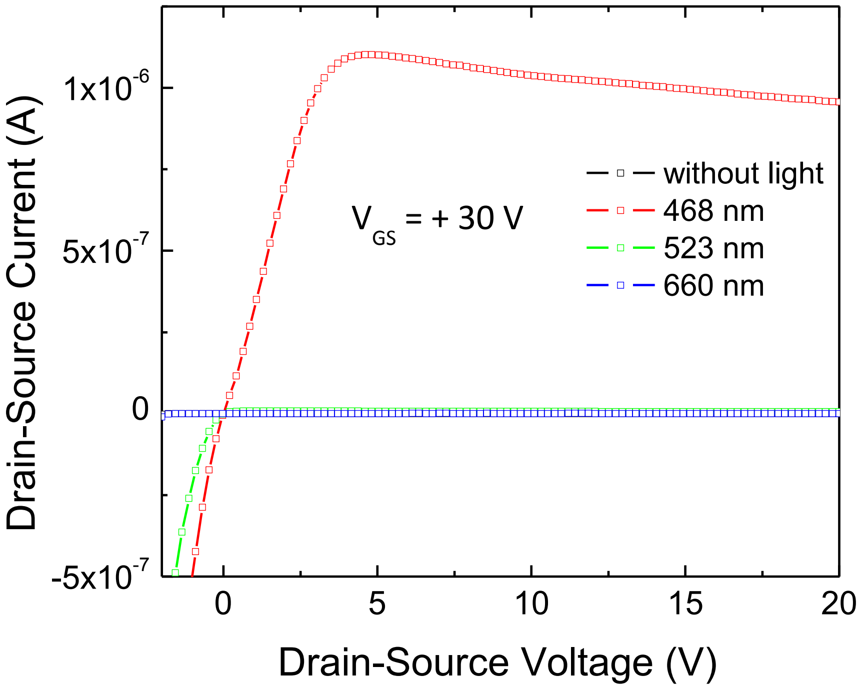


Figure 10.8. Output characteristic of the N-type (PTCDI-C_{13}) OTFT with several illuminations and V_{GS}= +30V

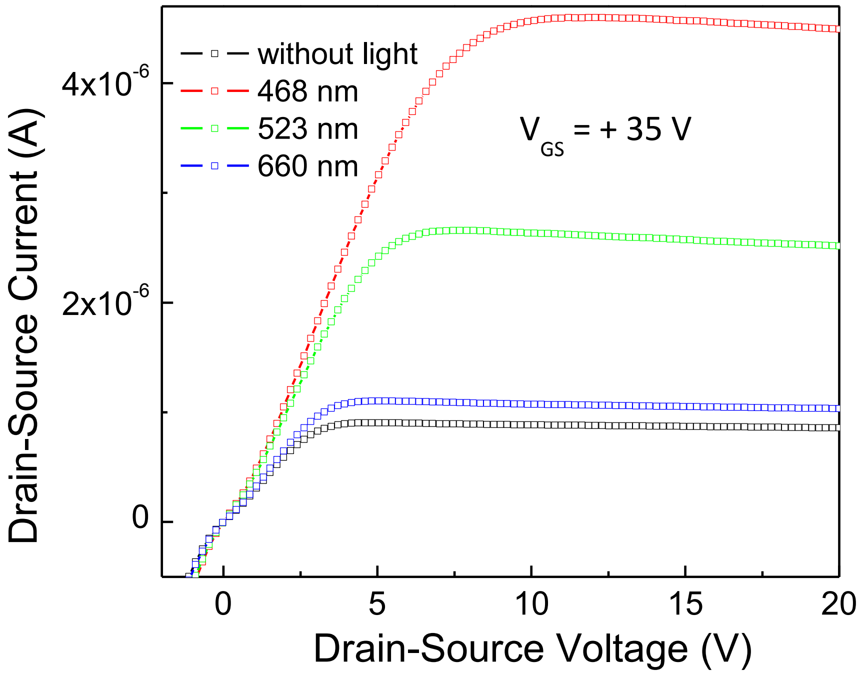


Figure 10.9. Output characteristic of the N-type (PTCDI-C_{13}) OTFT with several illuminations and V_{GS}= +35V

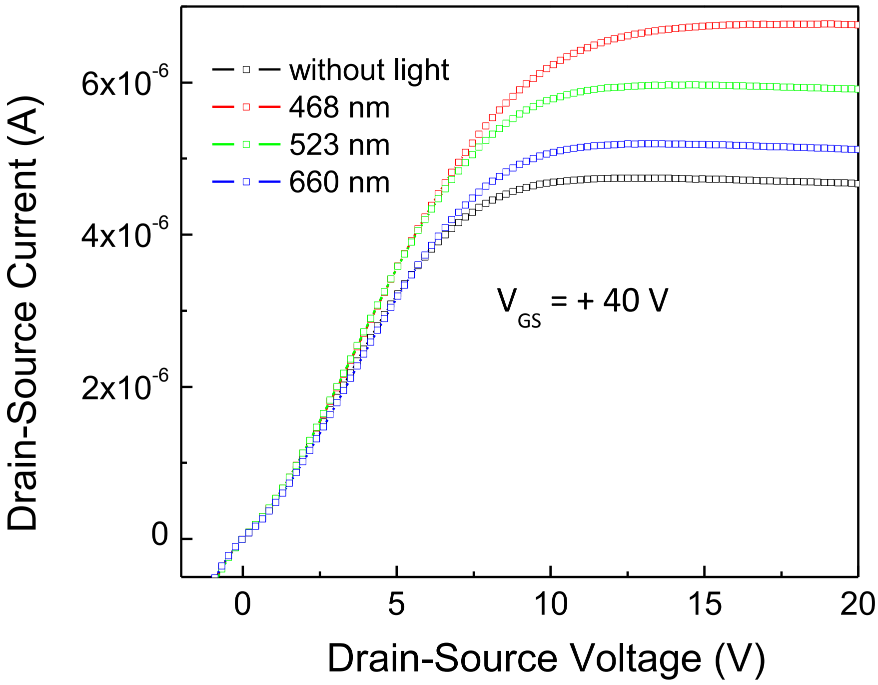


Figure 10.10. Output characteristic of the N-type (PTCDI-C_{13}) OTFT with several illuminations and V_{GS}= +40V

10.2.2.2 Transfer characteristic

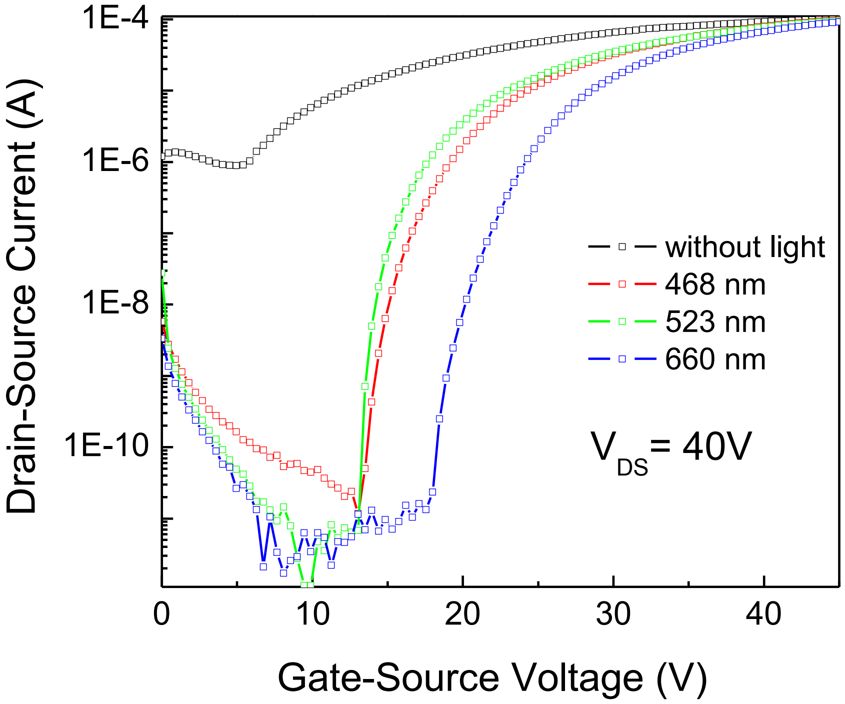


Figure 10.11. Transfer characteristic of the N-type (PTCDI-C_{13}) OTFT with several illuminations and V_{DS}= +40V

10.2.2.3 **Saturation characteristic**

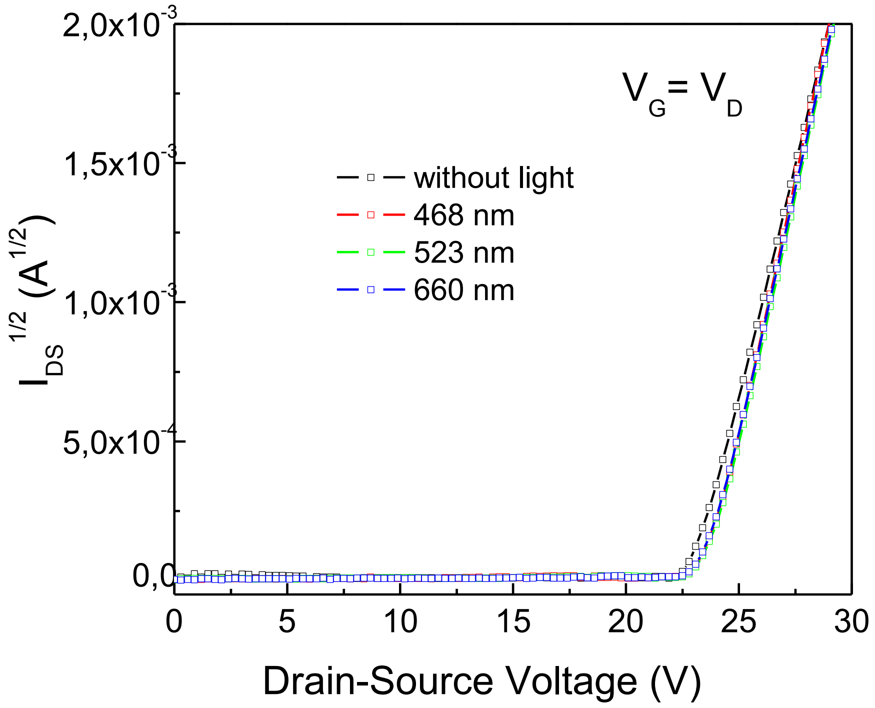


Figure 10.12. Saturation characteristic of the N-type (PTCDI-C_{13}) OTFT with several illuminations and V_G=V_D

10.2.3 Pentacene and PTCDI-C13

10.2.3.1 Output characteristic

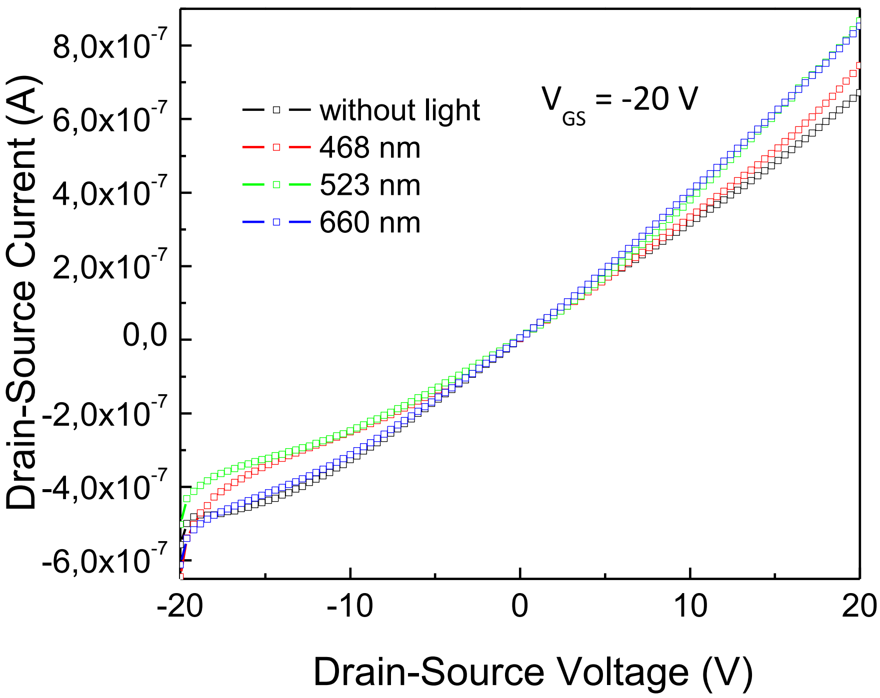


Figure 10.13. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{GS}= -20V

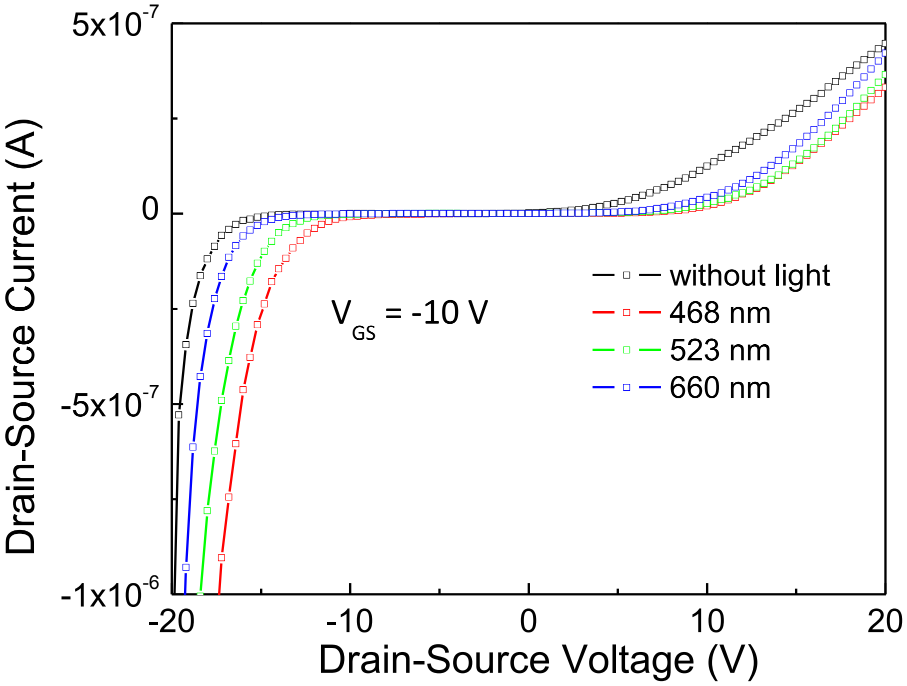


Figure 10.14. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{GS}= -10V

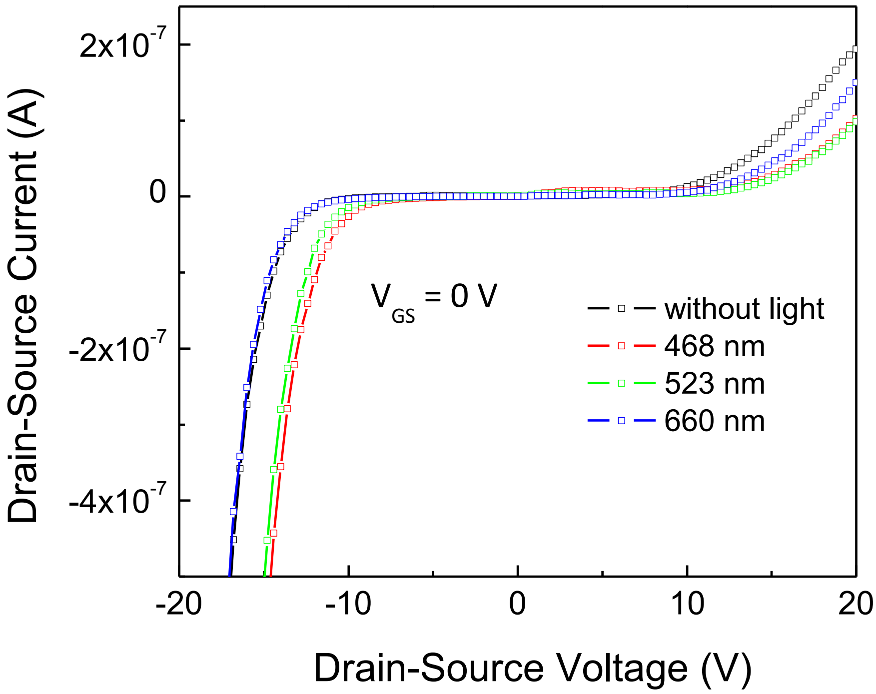


Figure 10.15. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{GS}= 0V

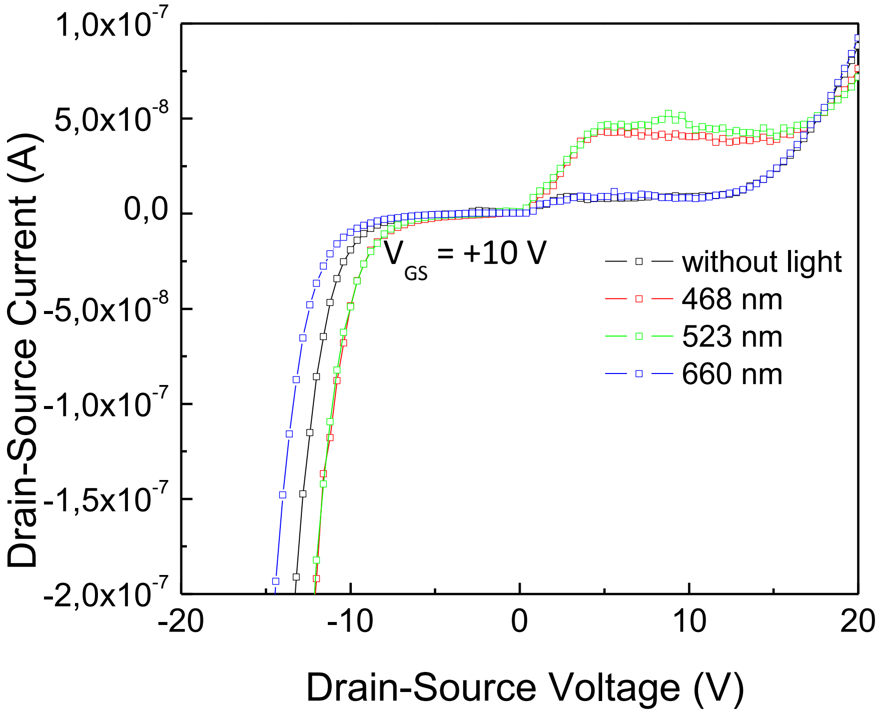


Figure 10.16. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{GS}= +10V

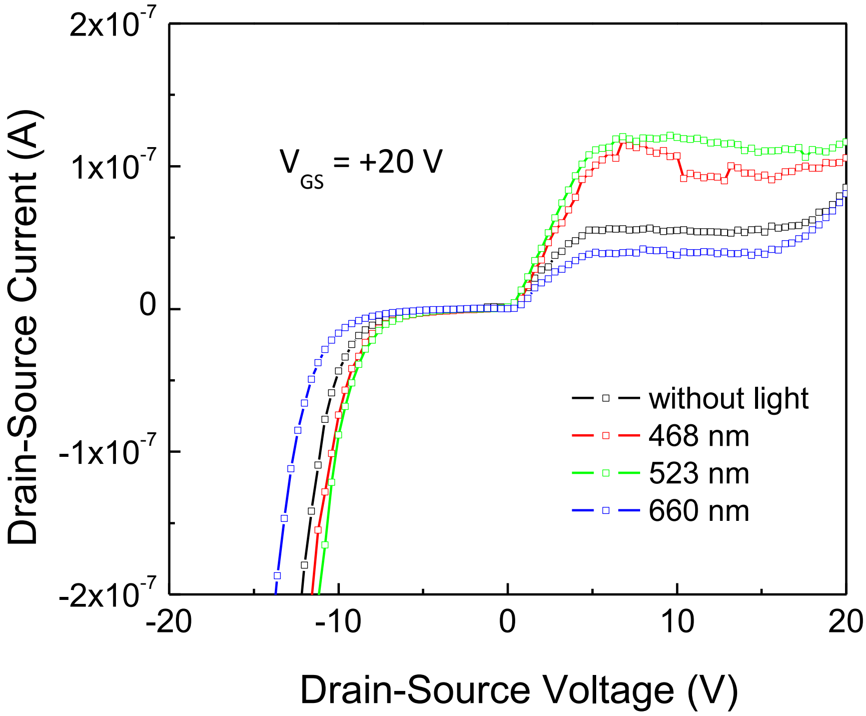


Figure 10.17. Output characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{GS}= +20V

10.2.3.2 Transfer characteristic

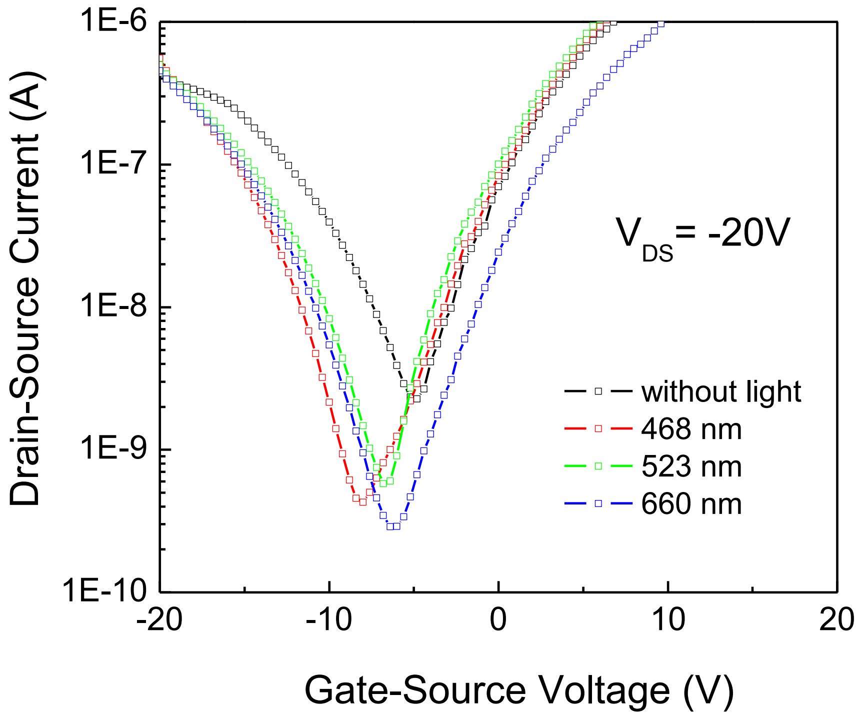


Figure 10.18. Transfer characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{DS}= -20V

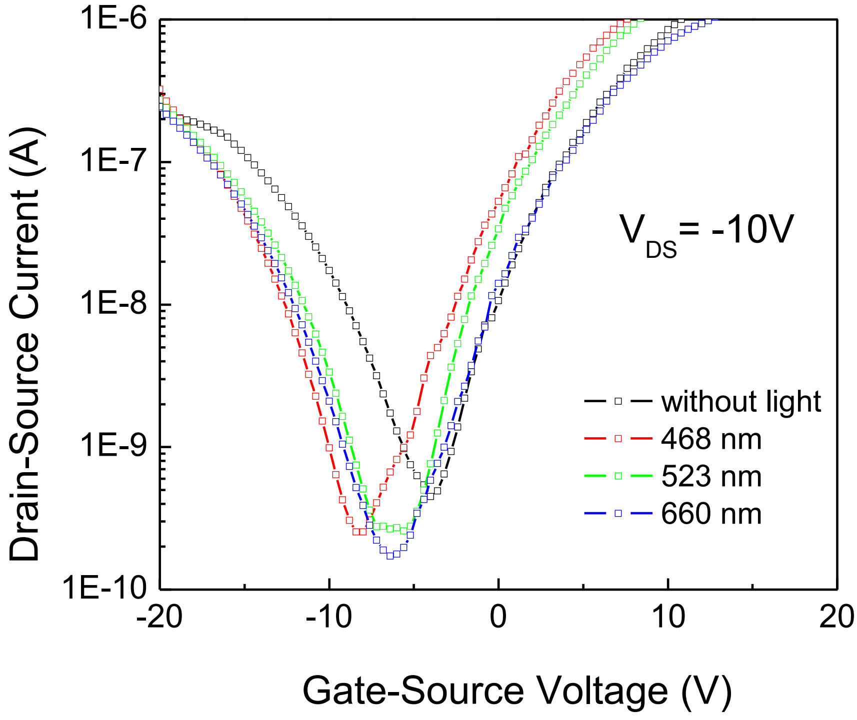


Figure 10.19. Transfer characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{DS}= -10V

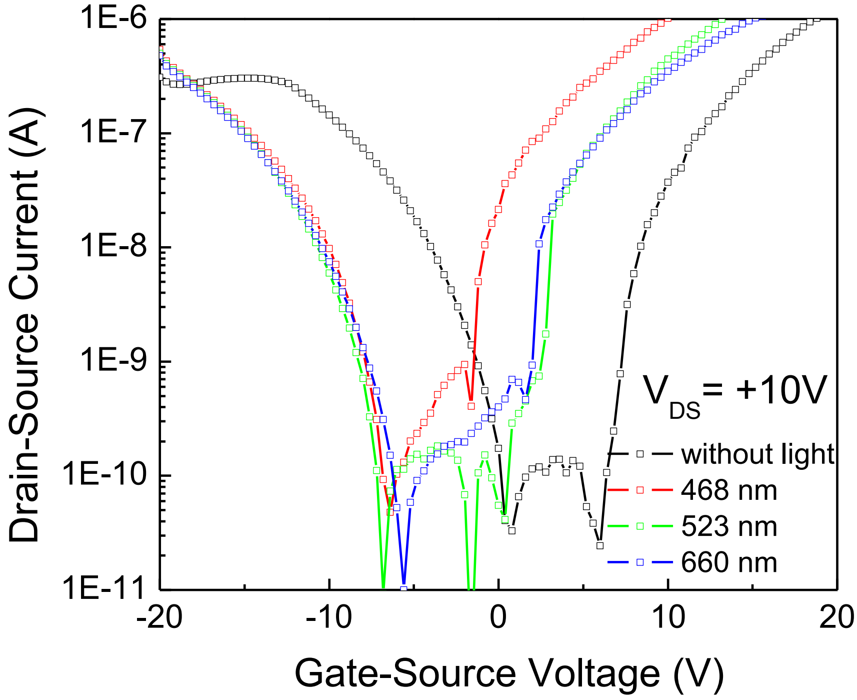


Figure 10.20. Transfer characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{DS}= +10V

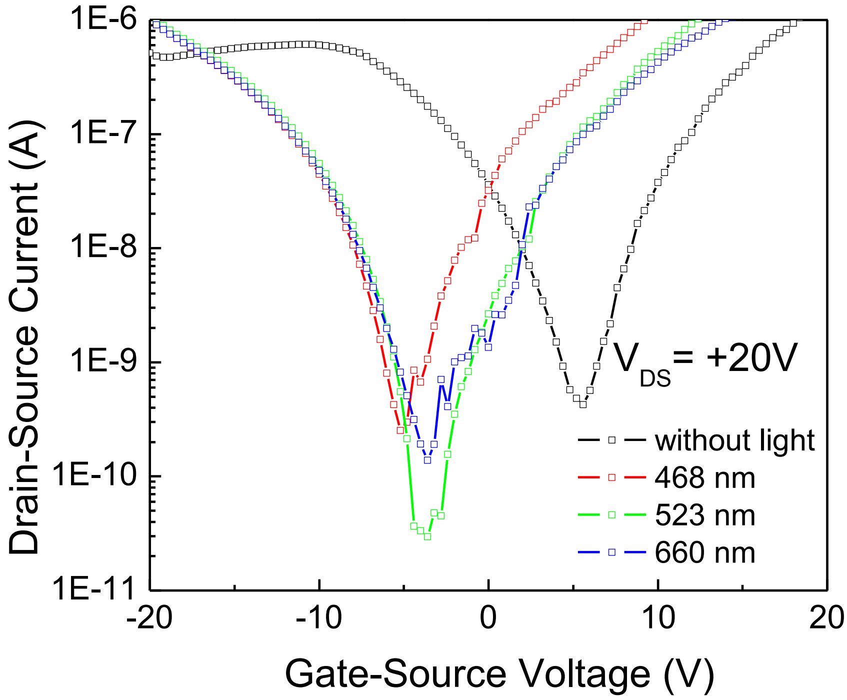


Figure 10.21. Transfer characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_{DS}= +20V

10.2.3.3 Saturation characteristic

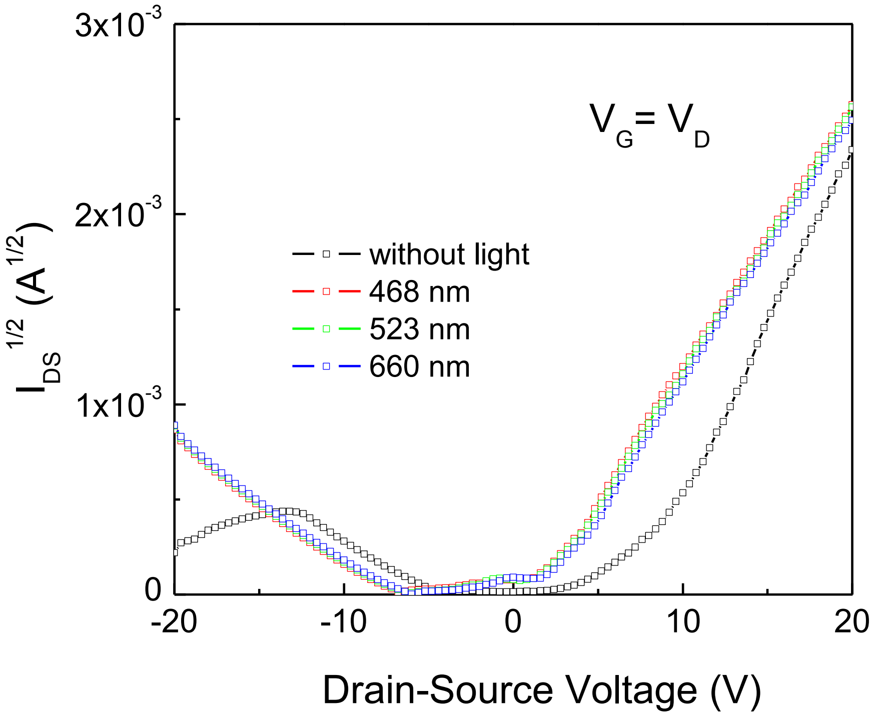


Figure 10.22. Saturation characteristic of the ambipolar OTFT with P-type and N-type semiconductors (pentacene and PTCDI-C_{13}), several illuminations and V_G=V_D

10.2.4 PTCDI-C_{13} and pentacene

10.2.4.1 Output characteristic

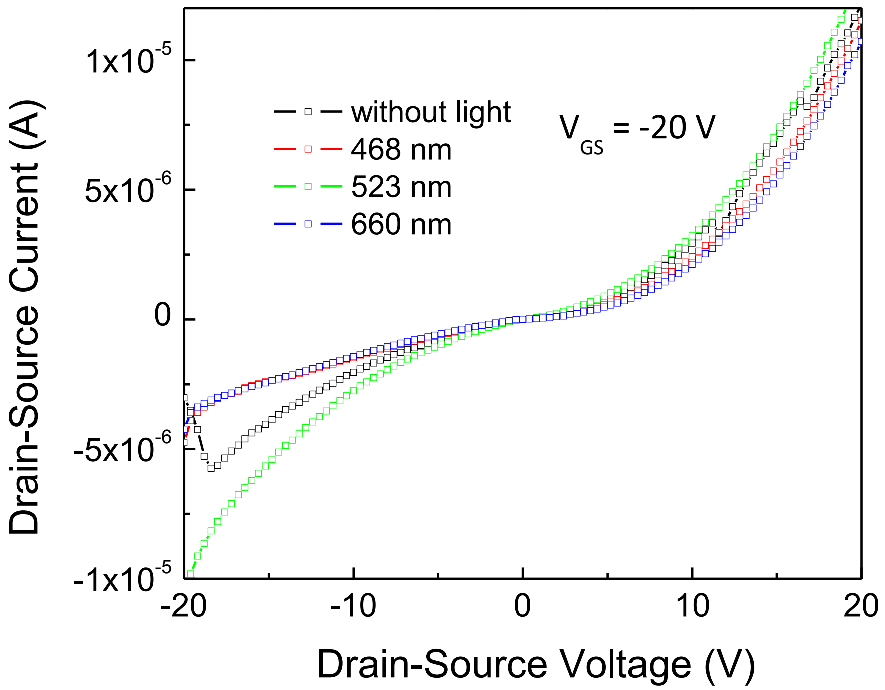


Figure 10.23. Output characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{GS}= -20V

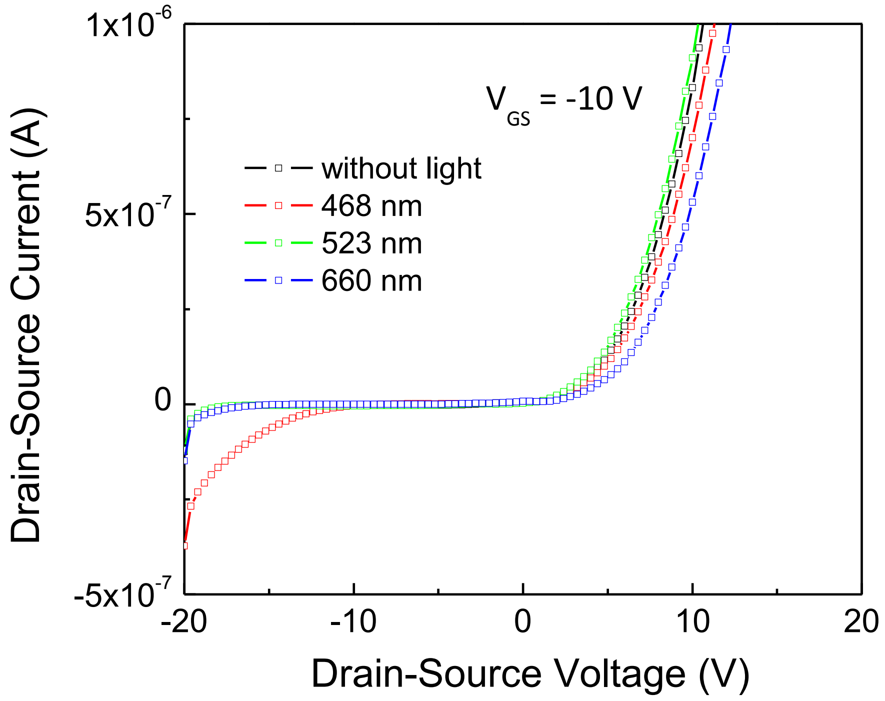


Figure 10.24. Output characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{GS}= -10V

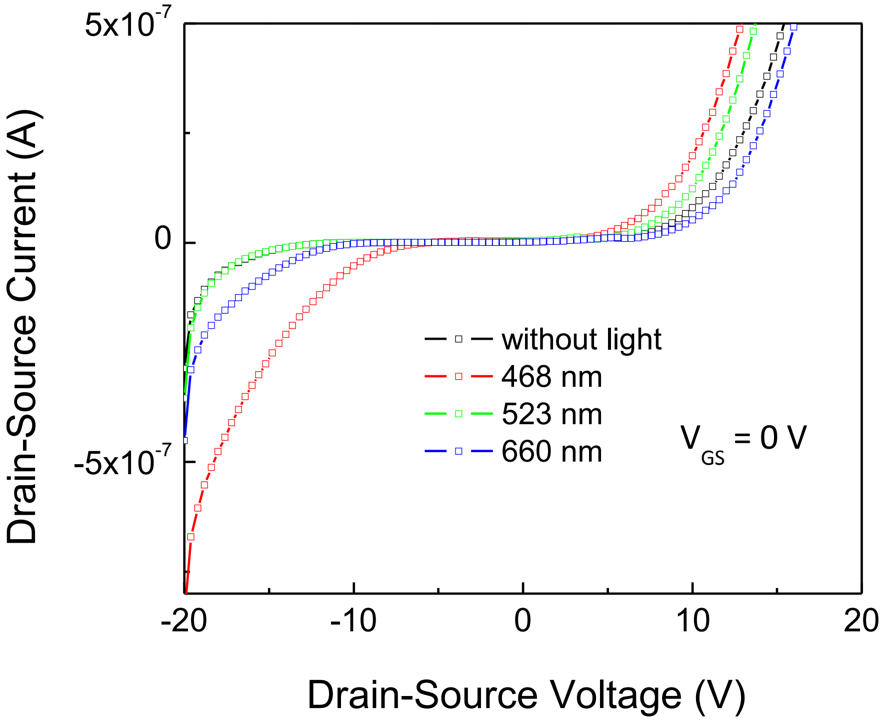


Figure 10.25. Output characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{GS}= 0V

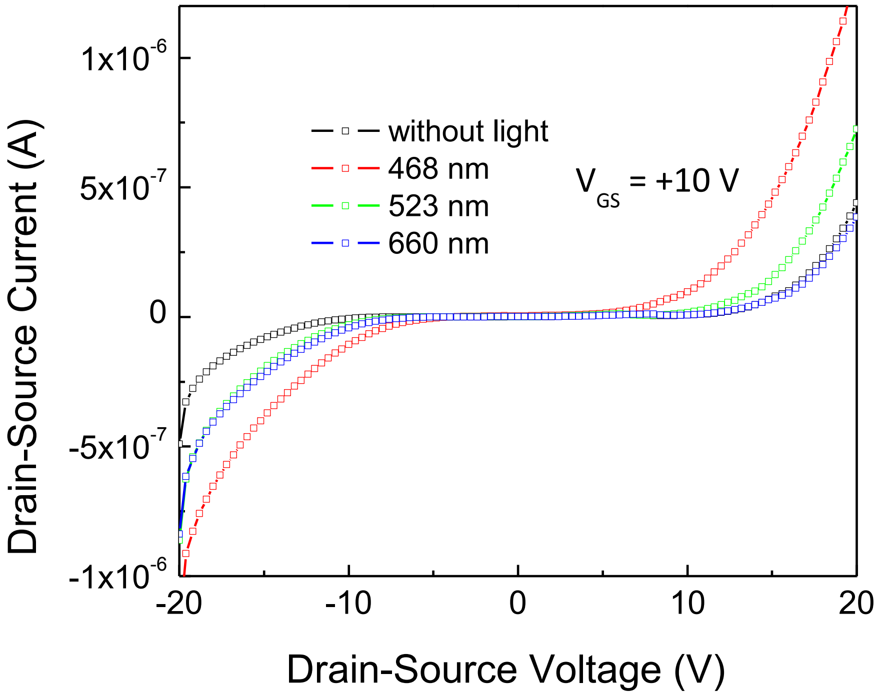


Figure 10.26. Output characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{GS}= +10V

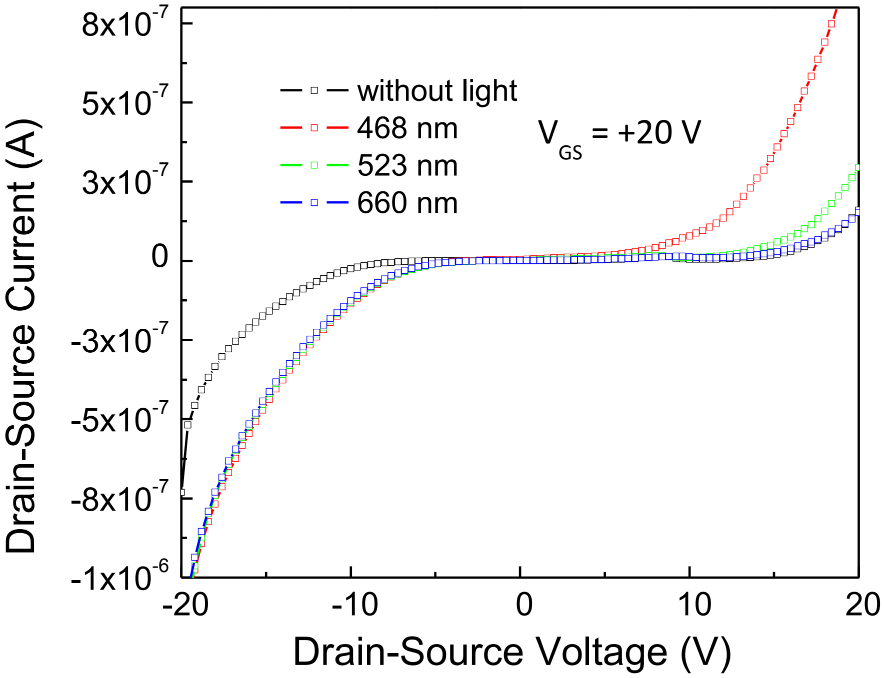


Figure 10.27. Output characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{GS}= +20V

10.2.4.2 Transfer characteristic

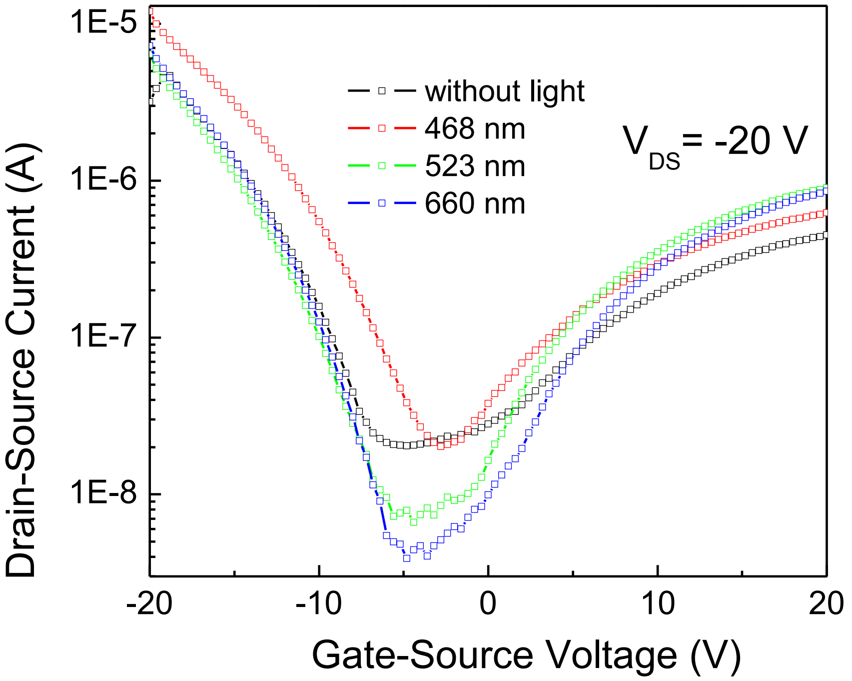


Figure 10.28. Transfer characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{DS}= -20V

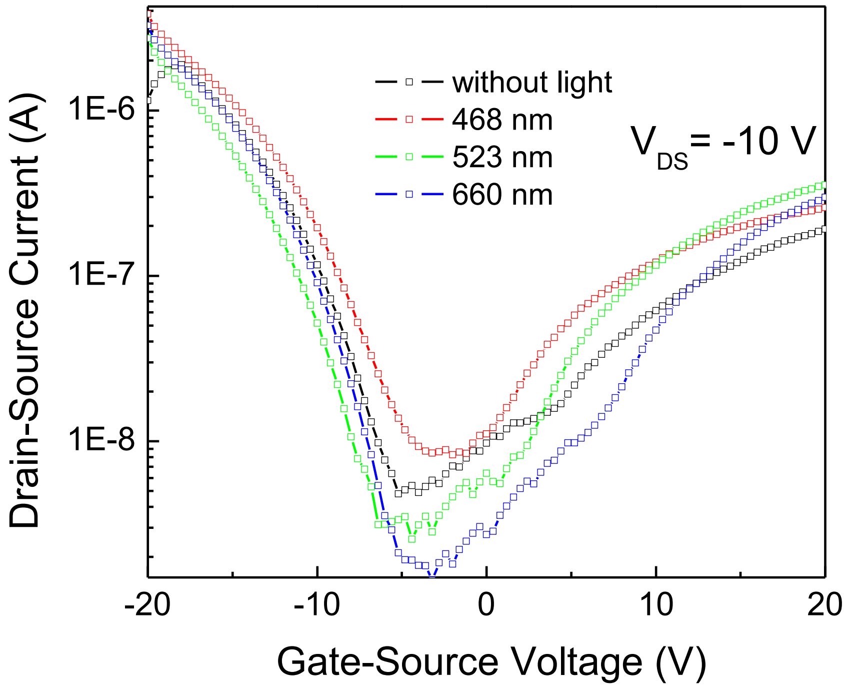


Figure 10.29. Transfer characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{DS}= -10V

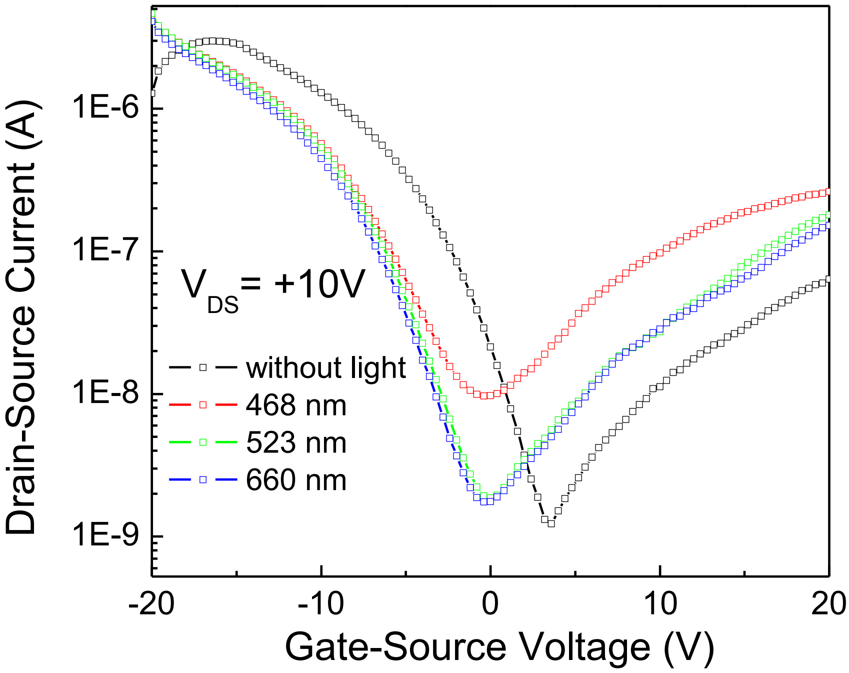


Figure 10.30. Transfer characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{DS}= +10V

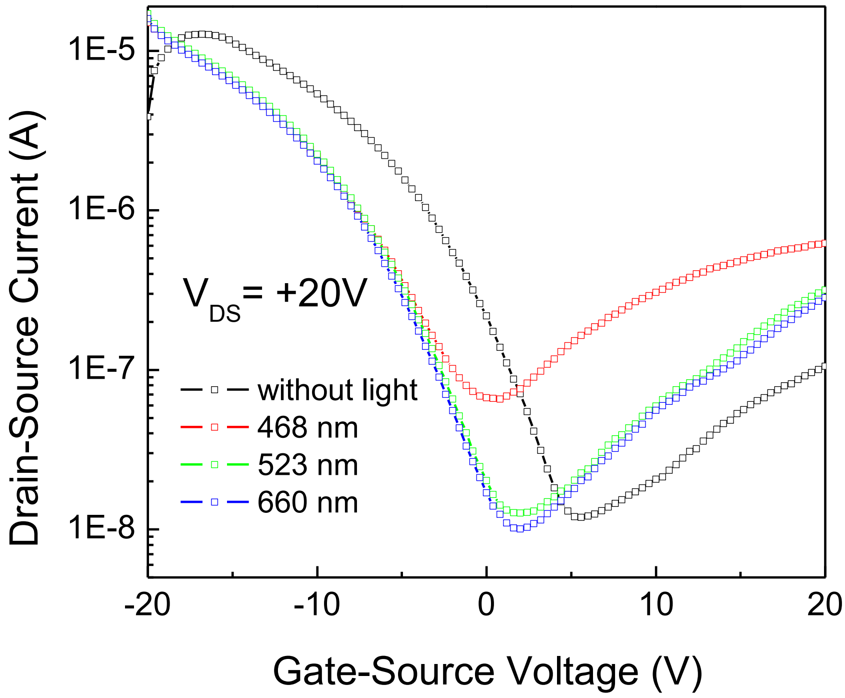


Figure 10.31. Transfer characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_{DS}= +20V

10.2.4.3 Saturation characteristic

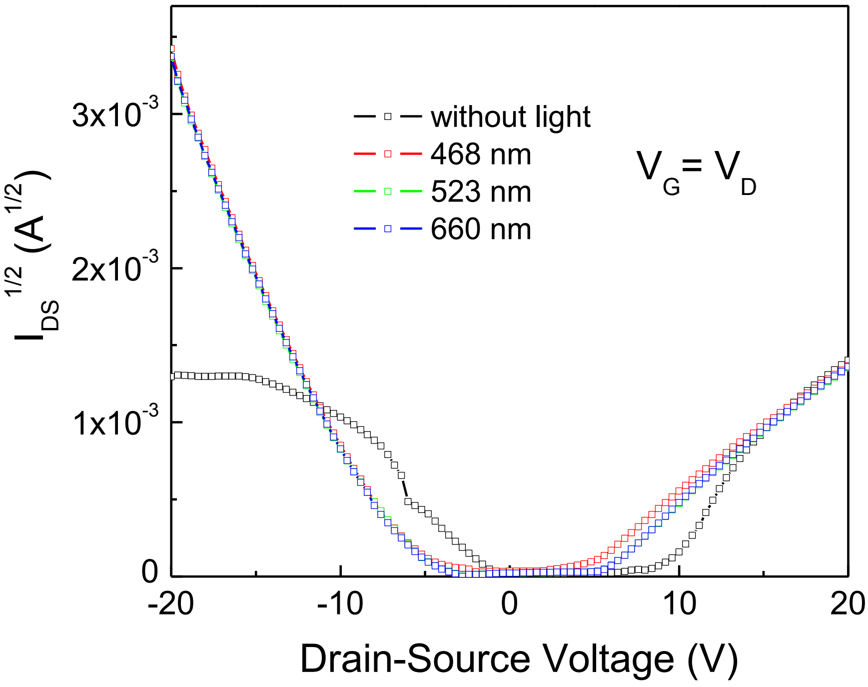


Figure 10.32. Saturation characteristic of the ambipolar OTFT with N-type and P-type semiconductors (PTCDI-C_{13} and pentacene), several illuminations and V_G=V_D

10.3 Results discussion

Concerning the two thin-film samples with only one type of semiconductors, it is clearly visible that the light absorbed by the semiconductor (see Figure 10.1) has an influence on the electrical characteristics of the devices. For example, in the output graph, the device shows a current much higher if the semiconductor absorbs the light projected on the device. To understand the generation of carriers in organic semiconductors is not easy. It is well known that in organic semiconductors light absorption creates excitons. These excitons diffuse in the bulk of the semiconductor, until they recombine. Diffusion length is reported to be around several tenths of nanometers before the exciton recombination.

As it was explained before to generate individual carriers it is needed to dissociate the excitons before they recombine. In the solar cell configuration this is done in the donor acceptor interface (where the acceptor accepts the electron and the donor donate the electron due to their IP and EA energy levels difference). In our case, in the individual TFTs without donor/acceptor it is not clear where the excitons are dissociated. The most probable place is in the metal semiconductor interface.

In the ambipolar case, the excitons would be mainly dissociated at the interface donor acceptor. But as explained in the preface, the ambipolar OTFTs study is much more difficult because the devices are composed of a heterostructure and that the behavior of organic materials are not yet well understood in this type of device.

Consequently, the graphs of the electrical characteristics of theses ambipolar devices have to be seen as an introduction for further study.

11 Conclusion

As reminder, the purpose of this final thesis was to study the behavior of two semiconductors (pentacene and PTCDI-C_{13}). The study was conducted by the realization of OTFTs (simple and with the two semiconductors) to see if it can be interesting to use it in devices as OTFTs or solar cells. The output, transfer and saturation characteristics have been studied without light to obtain the electrical characteristics. Finally, the samples were submitted to the lighting of different LEDs, chosen according to the wavelengths absorbed by the two semiconductor layers. Concerning illumination, it should be seen as an introduction to further study of this sort of sample.

The results analysis of the simple OTFTs are encouraging because of their good electrical characteristics. Regarding multilayer OTFTs, ambipolar behaviors were found, what is very interesting because it is able to conduce electrons and holes in accordance with the gate and drain voltages. All these results are very similar to what exists in the literature, which is very stimulating since all the samples were performed at low temperature.

Indeed, pentacene and PTCDI-C_{13} were deposited at respectively 150°C and 250°C. The innovation lies in the fact that these results were obtained with a dielectric (Al_2O_3) deposited at 150°C, what is very low compared to the temperature necessary to the deposition of SiO_2, usually about 1000°C.

Concerning the results with LEDs illumination on multilayer OTFTs, at this stage of progress we cannot make very accurate interpretations. Indeed, the semiconductors and their behaviors are not yet sufficiently understood since we are only at the first steps of research of this sort of devices. This part of the thesis has to be seen as an introduction to further study of this sort of sample. Nevertheless, we can already say that concerning simple OTFTS it is clearly visible that the absorption of light by the semiconductor excite the semiconductor molecules, increasing the number of charge carriers and consequently also the drain-source current.

Therefore, these materials offer great opportunities to develop devices with an interesting energy audit. This study opens possibilities for development and improvement. Better electrical characteristics can be researched by adjusting the manufacturing specifications.

12 Appendix

12.1 Appendix 1 : Pictures of OLEDs and their applications

Figure 12.1. Sony's flexible screen using OLEDs

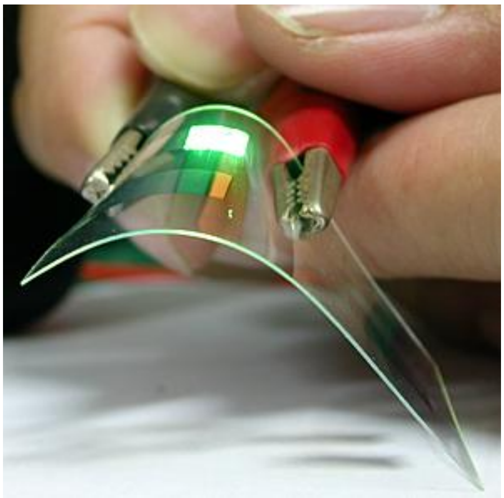


Figure 12.2. Sony's OLED with a thickness of 3mm

Figure 12.3. Sony's flexible screen using OLEDs

12.2 Appendix 1 : Pictures of OLEDs and their applications

Figure 12.4. Flexible solar panels using organic solar cells, by WILEY-VCH

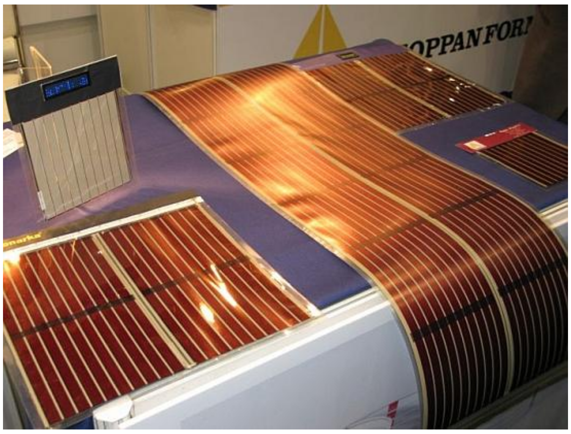


Figure 12.5. Flexible solar panels using organic solar cells, by Konarka

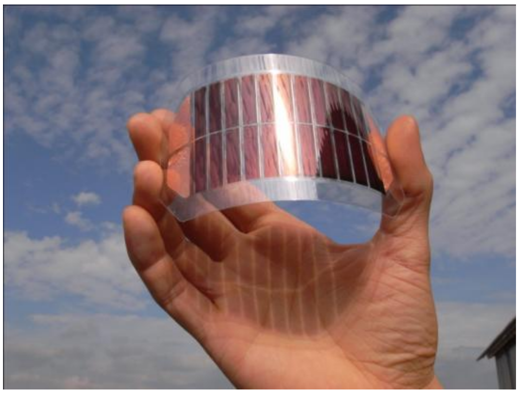


Figure 12.6. Flexible module of organic solar cells, by Eicke R.Weber

13 References

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