# Characterization of PEDOT:PSS deposited by inkjet printing

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**Abstract:** An Organic Light-Emitting Diode is made of organic layers on a glass or plastic structure. It emits light through the electroluminiscence effect. The use of inkjet printing technology for the fabrication of these devices has increased recently. This technology allows to reproduce patterns in a flexible substrate through drops of printing ink. In this study the properties for PEDOT:PSS, a material used for the Hole injection layer of OLEDs, were studied. Its properties in flexibility, transparency and conductivity were analyzed.

## I. INTRODUCTION

An *Organic Light-Emitting Diode* (OLEDs) is made of organic layers between two electrodes. The organic semiconductors are polymers or $\pi$-bonded molecules. The light emission is through the electroluminiscence effect. The electrons and holes, injected by the ohmic electrodes, recombine in the *Emission Layer* to form excitons. When these excitons are desexcited a photon is emitted and its wave length depends on the difference between the *Highest occupied molecular orbital* (HOMO) and the *Lowest unoccupied molecular orbital* (LUMO) levels. An advantage of OLEDs over LEDs is that they can be very thin and flexible due to the organic material characteristics. Moreover, OLEDs emit light diffusely and LEDs in a concentrated way [1]. The use of inkjet technology for the fabrication of these devices has a keen interest because of the higher local resolution and the less amount of material lost compared with other techniques.

In this work properties of PEDOT:PSS ink were studied. This ink is a polymer made up of two ionomers: poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate. It is normally used in OLEDs as *Hole injection layer*. This polymer has an special interest due to its flexibility, transparency and conductivity. Some different patterns were printed on a glass substrate to analyze the space resolution between two adjacent lines and to compare the perpendicular and parallel direction of printing. Furthermore, some lines were printed on a glass substrate without treatment and on a thin layer of gold in order to study the advantages of the surface. Moreover, some square layers with different width were printed to analyze changes in transmission when thickness increased. Finally, to be able to measure the conductivity some lines of PEDOT:PSS were printed on gold electrodes on a silicon substrate.

## II. THEORY

### A. Organic materials

Organic semiconductors are made up of $\pi$-bonded molecules or polymers composed of carbon and hydrogen atoms. The bonding occurs by $sp^2$ hybridization through an s and 2p orbitals to form 3 hybrid orbitals that form a strong bond with the neighboring carbon atoms ($\sigma$, $\sigma*$, the last one is more energetic). These are the ones that produce a certain stability, great hardness and elasticity. The $\pi$ and $\pi*$ (the last one is more energetic) bonds are formed by the pz orbitals between two carbon atoms. These two bonds are perpendicular to each other. The electrons in these pz orbitals are non localized and can move freely. Therefore, they are responsible for conductivity and semiconductor properties [2]. When the molecules are close enough, the proximity of the molecular orbitals results in a band distribution, due to this fact a separation between **HOMO** and **LUMO** energy levels occurs [3].

HOMO: Highest occupied molecular orbital in the polymer. Corresponds to the $\pi$ orbitals. In inorganic semiconductors its equivalent would be the valence band. LUMO: The lowest unoccupied molecular orbitals. They correspond to the $\pi*$ orbitals. In inorganic semiconductors its equivalent would be the conduction band.

These two energy levels are separated by a larger energy gap than in the inorganic case. This energy makes organic materials generally insulating, but they exhibit semiconductor behavior when carriers are injected from electrodes or are generated by doping.

In addition, the different molecules interact with each other with Van der Waal bonds, weaker than the covalent bonding of inorganic semiconductors. Therefore, the disorder of organic materials is governed by these weak interactions that make it difficult the overlap between orbitals that could lead to a band structure as in the inorganic case. Taken into account the disordered structure and the weak interaction between molecules, the transport of charge takes place in non localized HOMO and LUMO bands. The electric charge is concentrated in molecular entities and the transport occurs by hopping between segments of the polymer [4] . This charge transport occurs through electron transfer between levels located between nearby molecules. The environment of the orbitals of each molecule plays an important role in its energy. Therefore, this is also an explanation of why we do not have well-defined levels of HOMO and LUMO, but rather the density of states takes on a Gaussian distribution. One consequence of this charge transport mechanism is that the mobility is some orders lower than in inorganic semiconductors [2]. These organic semiconductors are used in a wide range of optoelectronics applications due too their mechanical flexibility their low cost and easy manufacture. Some of the manufactured devices are OLEDs, organic solar cells and *organic field-effect transistor* (OFET).

### B. OLED (organic Light-Emmiting Diode)

An OLED is an organic LED that emits light by itself. It consists of a series of organic layers between two electrodes. Light emission occurs due to the recombination of electrons and holes injected by ohmic electrodes.

Holes are injected from the anode with a large work function and electrons from the cathode with a small work function as long as we are in positive polarization. One of the two electrodes must be transparent in order to allow the output of the light generated in the recombination of pairs of electrons-holes.

Description of the layers (all of them must allow the transmission of the emitted wavelength) [3, 4]:

**Anode**: *Indium Tin Oxide* (ITO) is the common material used as anode, since it is a transparent electrode and allows a high efficiency of light extraction. Materials such as PEDOT, polynonine and polypyrrals can also be used as they are also transparent.

**HIL**: *Hole injection layer*: Its function is to low the holes injection's barrier, since it presents a work function independent and bigger than the one of the ITO. In addition, it also allows us to have no direct contact between the ITO and the HTL, avoiding a diffusion current of species that have oxygen from the ITO to the HTL, therefore, the life time of the device increases. Normally, for this layer the PEDOT:PSS is used because it is transparent and conductive.

**HTL**: *Hole transport layer*: It must have high holes' mobility and avoid drift current (prevent electrons from the anode from reaching the cathode).

**EML**: *Emission layer*: It presents specific HOMO and LUMO in order to facilitate the injection of holes and electrons from the adjacent layers, as well as a high photoluminescence. In this layer the recombination of the injected electrons and holes travelling in opposite senses takes place and they can do it radioactively and emit light (electroluminescence).

**ETL**:*Electron transport layer*: It must have a high mobility of electrons and avoid drift current (prevent holes in the cathode from reaching the anode).

**EIL**: *Electron injection layer*: It must have properties similar to HIL, but for electrons. Optimal materials would be Ca, Ba and Mg but these are reactive to moisture. Therefore, Al is the most used material.

**Cathode**: The material usually used is Liq as it has a low work function.

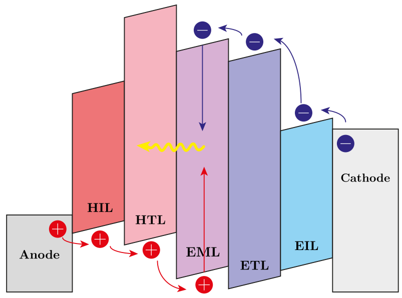


FIG. 1: Representation of the OLEDs energy band structure.

In order to **generate light**, in the EML layer the electrons and holes recombine to form excitons. The wave lenght of the emitted photon depend on the distance between HOMO and LUMO levels of the electoluminiscence molecule that forms the layer. In general, in organic molecules only the singlet state of energy can emit radioactively and the 25% of excitons generated are emitted radioactively [4]. This leads to not very high efficiency. However, it was discovered that if the organic semiconductor was doped with a phosphorescent ink with a strong spin-orbit coupling, the triplet states also emit thus increasing efficiency. Because of a much narrower emission is achieved a high spectral purity can be achieved.

To truly understand the **carrier injection**, it must be taken into account the injection barrier, which is the difference between the work function of the anode and the HOMO of HTL, and the difference between the work function of the cathode and the LUMO of the *Electron transport layer* (ETL). There are two models for explaining how carriers cross barriers: Fouler-Nordheim field emission tunneling and the Thermionic emission taking into account the backlow [2]. The combination of these models fits quite well with reality. With an ohmic contact, the injection barrier can be reduced [3]. Therefore, the work function of the anode should be similar to the HOMO level of the HTL and the work function of the cathode to the LUMO level of ETL.

### C. PEDOT:PSS

PEDOT:PSS is transparent, conductive, flexible and has a low temperature process. These features lead to this polymer to be used in OLEDs and others flexible electronic devices.

As mentioned earlier in the case of OLED it can be used as an anode to form the HIL and HTL layers. It is intended to replace ITO as there are no large abundances of indium. On the other hand, it has less conductivity than ITO, although it can be increased by doping. When more layers of this ink is printed, more conductive is the material but less transparent. It is important to find the balance between these two properties for each application [5].

### D. Fabrication with inkjet printing

The inkjet technique has many advantages over standard techniques such as spin-coating, and is gaining importance in the manufacture of such devices. With the spin-coating technique a lot of material is lost, and even though it covers the whole surface, it has low spatial resolution. The lithography technique is used to remove the coating in specific areas, but this involves more steps in the process, more difficulties as the number of layers increases and more cost. On the other hand, inkjet printing allows you to deposit material in specific places without the use of lithography, less material is lost and it is cheaper. In addition, it is a fast, non-contact technique, versatile and compatible with a wide variety of materials [6].

## III. CHARACTERIZATION

The purpose of this work is to study the PEDOT:PSS (AI 4083) ink from Ossila. In order to study different properties of this material, some patterns were designed [7]. These patterns can be seen in Fig. 2. The structure (a) tests the different nominal width of printable lines from 75 to 145 $\mu$m with steps of 30 $\mu$m. The pattern (b) tests the space resolution between two adjacent lines of nominal width 330 $\mu$m and length 1000 $\mu$m, orientated in the print direction. The spacing between the two lines was increasing form 75 $\mu$m to 345 $\mu$m with steps of 30 $\mu$m. The structure (c) tests the quality of the printed in the perpendicular direction. The pattern (d) tests the transmission of the light through a layer with different thickness. It also tests the capability to print full areas. The morphology was analysed in Institut de Bioenginyeria de Cataluya (IBEC) with a profilometre from the manufacturer Bruker, model DEKTAK XT. The transmission of the films were analyzed in Centres Científics i Tecnològics UB (CCiT) with ultraviolate-visible spectrometer SPECORD 205. The uniformity of the films were analyzed with the Scanning Electron Microscope (SEM), ESEM-VPSEM Quanta 200 in CCiT.

### A. Printing and substrate treatment

For the printing the device Dimatrix DMP-2830 was used. The drop spacing was set to the value of 30 $\mu$m and no heating for the printhead was applied (T=28ºC). This drop spacing was almost the radius of the drop's ink. 10 pl printheads were used to determine the printed volume. No temperature at the platen was applied. The firing voltages were those that allowed the printing drops to achieve the velocity of 6 $\mu$m/s. The distance between the substrate and the nozzle was set to 650 $\mu$m. It was important to adjust the velocity of the drops with the distance to avoid satellite drops and the drop's spreading. The ink used was not prepared for inkjet printing. Due to this fact, sometimes the nozzles were clogged. To unblock them, the cartridge was sonicated for 5 minutes with the same ink.

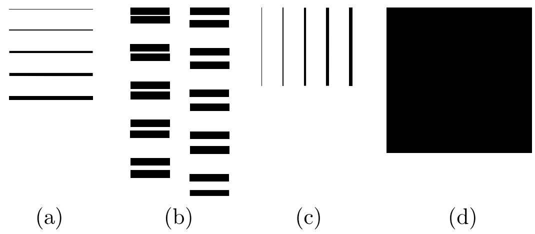


FIG. 2: Patterns used to characterize some properties of PEDOT:PSS.

The different structures were printed on a glass substrate. The wettability of the ink depended on the substrate treatment. The ink spreading behavior was attributed to the low surface energy of the substrate. The following steps were applied to improve the wettability of ink on the glass substrate:

1. The substrate was cleaned with isopropanol.

2. UV-Ozo treatment for 12 minutes (with a UV Ozone Cleaner from Ossila) .

3. Pressure $N_2$ blow to eliminate the residual particles.

With this preparation the drop on the surface had the diameter of 75 $\mu$m. In the glass substrate without treatment was 53 $\mu$m and in a gold thin layer it was 38 $\mu$m.

## IV. RESULT AND DISCUSSION

### A. Width of printable lines

To study this section the pattern (a) of Fig. 2 was used. In Fig. 3 it can be seen that the width of printed line is higher than the nominal line width. The nominal width was calculated taking into account the drop spacing, the diameter (D) of the drop and that 1 pixel is one drop: $w_n$ = (number of pixels) $\cdot$ Drop Spacing + $D$. This discrepancy is due to the overlapping of the drops, which causes a higher spreading, which is not included in the nominal width equation. The fit can approximately predict the real width of the printed lines.

### B. Space resolution between two adjacent lines

For this study the structure (b) from Fig. 2 was used. The profilometer technique was used to determine the smallest resolvable distance between two adjacent lines. The separation was measured in the centre of the line. This distance was resolved up to 4 $\mu$m that corresponds to a nominal distance of 135 $\mu$m. The distances corresponding to 165 and 195 $\mu$m were 12 $\mu$m and 38 $\mu$m. In Fig. 4 are represented the obtained results.

It was appreciated that below the nominal distance of 135 $\mu$m between 2 lines, the lines were not distinguish-

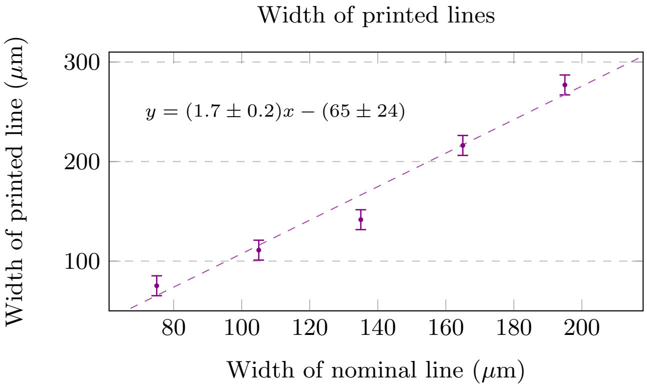


FIG. 3: Representation of the dependence of the width of printed line with the nominal line width.

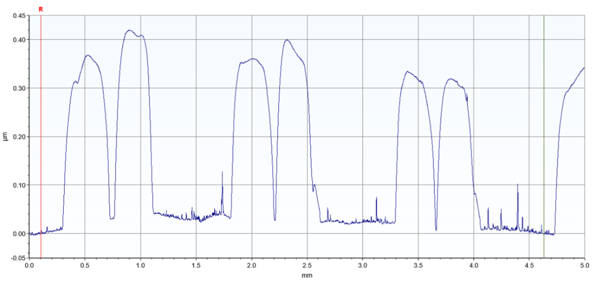

FIG. 4: Morphology of adjacent lines spaced of 135, 165 and 195 $\mu$m measured with the profilometer technique.

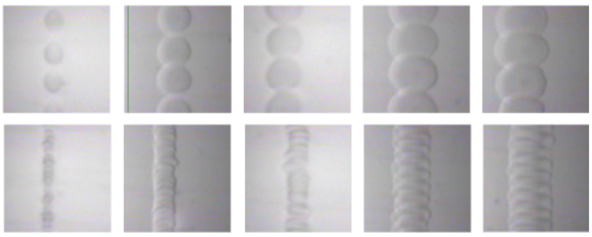

FIG. 5: Image obtained with the profilometer technique of 5 lines in the perpendicular direction of printing using 4 (up) and 1 nozzle (down).

able. Due to the fact that a line of nominal width of 345 $\mu$m had a huge amount of matter, the nominal distance is smaller than the real distance because the lines had the tendency of spread the matter.

### C. Perpendicular direction of printing

For this study, the structure (c) from Fig. 2 was used. In Fig. 5 are shown the printed lines in the perpendicular direction using 4 nozzles (first row) and 1 nozzle (second row). Comparing these two cases it was seen that the drops that were thrown at the same time, tended to gather and did not interact with the previous deposited drops. Due to this fact, they occupied less space than they should. That is why the different group of drops using 4 nozzles are not attached. On the opposite site, using only one nozzle this effect was not observed because only one drop was thrown each time. To confirm this hypothesis a line in the direction parallel to the movement of the printhead was made in 4 steps, and a similar result was obtained.

### D. Transmission of the light throw a fine film

The structure (d) from Fig. 2 was used to study the transmission. To analyze the dependence of the transmission with the thickness, four films of nominal width of 6340 $\mu$m with different number of layers (from 1 to 4) were made. To obtain a uniform film it was necessary to increase the drop spacing to 35 $\mu$m and the temperature of the platen to 35ºC. The drop spacing was increased to reduce the accumulated ink and the increase of the temperature was necessary to dry faster the film and to establish it. With a space dropping of 20 $\mu$m the capillarity force made that the drops were accumulated. The time between prints were 5 minutes and 6 nozzles were used. With the profilometre it was noticed that the layer's edge of the film had a slightly higher thickness that the rest of the square. The reason of that it was suggested to be the *coffee ring effect*. At the central part of the layer this effect is not observable and we obtained a uniform layer. This effect is caused by the fast evaporation rate at the edge of the drop. Due to the capillarity flow to supply the solvent for this evaporation a ring shape is formed at the edge [8]. The results are exposed in Fig. 6 and in the table I. It was observed that transmittance decreased when the thickness increased. Nevertheless, for all the analyzed thicknesses a transmittance over 85%, centered in the blue spectrum, was observed.

With a Scanning Electron Microscope the morphology of the films were analyzed. It could be conclude that uniform films were made without holes of ink. In the Fig.7 the result can be seen in a scale of 100 $\mu$m.

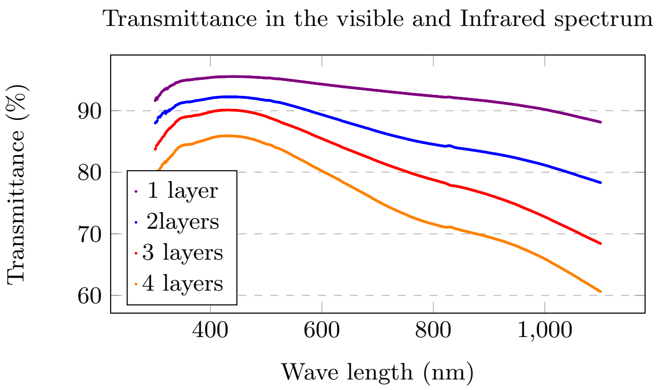


FIG. 6: Representation of the transmittance of the different layers in the visible and infrared spectrum.

| **Layers** | **Thickness** $\pm0.001(\mu m)$ | $\mathbf{T}(\%)(\pm0.1)$ | $\boldsymbol{\lambda}(\pm10)$ (nm) |
|---|---|---|---|
| 1 | 0.156 | 95.6 | 445 |
| 2 | 0.244 | 92.3 | 434 |
| 3 | 0.528 | 90.1 | 431 |
| 4 | 0.629 | 85.9 | 437 |

TABLE I: Number of layers, its thickness, its maximum transmittance and the wave length of the maximum transmittance.

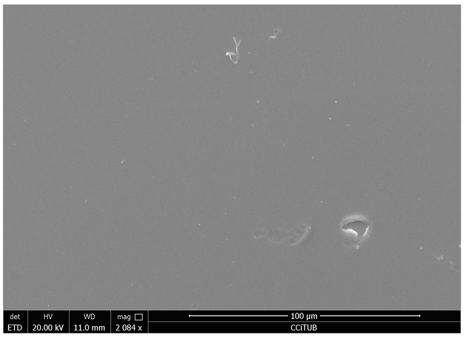


FIG. 7: Image made with a SEM of a uniform film of 4 layers.

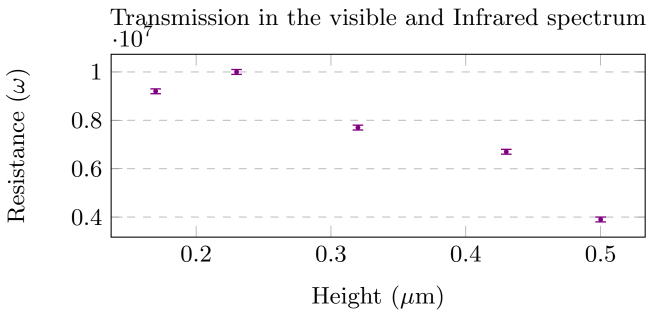


FIG. 8: Representation of the dependence of the resistance with the thickness. Data obtained with the two points probe.

### E. Dependence of resistance as function of height

In order to analyze the resistance, the ink was printed on some gold electrodes on a silicon substrate. Owning to the difference wettability of gold and silicon, not all the printed lines were correctly printed. The ink presented the tendency to be deposited on the silicon. Nevertheless, some lines with different thickness could be printed and analyzed with the two points probe. It was observed that the resistance reached its stable value 4 seconds after the voltage was applied. It could be seen in Fig. 8 that the resistance decreased when the thickness of the line increased. To determine the resistivity, the area of the printed lines were approximated with the data of the profilometre. The manufacture fix the resistivity in a range of 500-5000 $\Omega$ cm. The resistivity obtained was over the limit bellow, around 500 $\Omega$ cm.

## V. CONCLUSION

This work centred its research in the inkjet printing technology. Using this technique, PEDOT:PSS had been printed, this is an organic semiconductor used in the HIL of OLEDs.

Different patterns to print were designed to analyze different characteristics of this material and technique. The processing parameters were optimized in order to produce uniform and continuous stable films with controlled thickness. The distance between two adjacent lines was resolved up to 4 $\mu$m. This demonstrate the high spacial resolution of this technique. Moreover, it was seen that the printing direction had a significant influence in the results. It was also proven that PEDOT:PSS had a great transmittance, even with 4 layers of thickness it is above 85%. It was seen that this material is transparent in the visible spectrum. This feature is ideal for its use in the HIL layer and as a substitute for ITO in transparent anodes. The resistivity obtained was around 500 $\Omega$ cm that fits the manufacturer specifications (500-5000 $\Omega$ cm). Hence, this material without being doped is not usually very conductive. To work as HIL a higher conductivity is needed. With proper doping, as seen in [6] the conductivity increases considerably.

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