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Analysis of the current-voltage characteristics of polymer-based organic light-emitting diodes (OLEDs) deposited by spin coating

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Abstract

Polymer-based organic light-emitting diodes (OLEDs) with the structure ITO / PEDOT:PSS / MDMO-PPV / Metal were prepared by spin coating. It is known that electroluminescence of these devices is strongly dependent on the material used as cathode and on the deposition parameters of the polymer electroluminescent layer MDMO-PPV. **Objective.** In this work the effect of i) the frequency of the spin coater (1000-8000 rpm), ii) the concentration of the MDMO-PPV: Toluene solution, and iii) the material used as cathode (Aluminium or Silver) on the electrical response of the devices, was evaluated through current-voltage (I-V) measurements. **Materials and methods**. PEDOT:PPS and MDMO-PPV organic layers were deposited by spin coating on ITO substrates, and the OLED structure was completed with cathodes of aluminium and silver. The electric response of the devices was evaluated based on the I-V characteristics. **Results.** Diodes prepared with thinner organic films allow higher currents at lower voltages; this can be achieved either by increasing the frequency of the spin coater or by using concentrations of MDMO-PPV: Toluene lower than 2% weight. A fit of the experimental data showed that the diodes have two contributions to the current. The first one is attributed to parasitic currents between anode and cathode, and the other one is a parallel current through the organic layer, in which the carrier injection mechanism is mediated by thermionic emission. Conclusions. The results of the fitting and the energy level alignment through the whole structure show that PPV-based OLEDs are unipolar devices, with current mainly attributed to hole transport.

Key words: organic semiconductors, OLEDs, electroluminescent polymers, MDMO-PPV, PEDOT:PSS, Spin coating, HOMO, LUMO, carrier injection, thermionic emission.

Resumen

Análisis de la característica corriente-voltaje de diodos orgánicos emisores de luz (OLEDs) basados en polímeros depositados por *spin coating*. Se fabricaron diodos orgánicos emisores de luz (OLEDs) con la estructura ITO / PEDOT:PSS / MDMO-PPV / Metal mediante la técnica de *spin coating*. Es ampliamente conocido que la electroluminiscencia de estos diodos depende fuertemente del material usado como cátodo y también de los parámetros de crecimiento de la capa del polímero electroluminiscente MDMO-PPV. **Objetivo.** En este trabajo el efecto de i) la frecuencia del *spin coater* (1000-8000 rpm), ii) la concentración de la solución MDMO-PPV: Tolueno y iii) el material usado como cátodo (plata o aluminio) sobre la repuesta eléctrica de los dispositivos, fue evaluado a través de medidas de corriente-voltaje (I-V). **Materiales y métodos.** Películas delgadas de los materiales orgánicos PEDOT:PSS y MDMO-PPV fueron depositados por *spin coating* sobre sustratos de ITO, y la estructura del OLED fue terminada con cátodo de plata y aluminio. La respuesta eléctrica de los dispositivos fue evaluada a través de su característica I-V. **Resultados.** Los diodos fabricados con películas orgánicas más delgadas son los que suministran mayores corrientes a menores voltajes. Esto puede lograrse ya sea incrementando la frecuencia de rotación del *spin coating* o usando concentraciones de MDMO-PPV: Tolueno menores al 2% en peso. Un ajuste de los datos experimentales demostró que los diodos poseen contribuciones de una corriente parásita entre ánodo y cátodo, y otra corriente paralela en donde el mecanismo predominante de inyección de portadores a la capa orgánica es a través de emisión termoiónica. **Conclusiones.** El ajuste de los datos experimentales, junto con la posición de niveles de energía a través de la heteroestructura, demuestra que los OLEDs basados en derivados de PPV son dispositivos unipolares, en el que la corriente se atribuye principalmente a transporte de huecos.

Palabras clave: semiconductores orgánicos, OLEDs, polímeros electroluminiscentes, MDMO-PPV, PEDOT:PSS, Spin coating, HOMO, LUMO, inyección de portadores, emisión termoiónica.

Resumo

Análise da característica corrente-voltagem de diodos orgânicos emissores de luz (OLEDs) baseados em polímeros depositados por spin coating. Foram fabricados diodos orgânicos emissores de luz (OLEDs) com a estrutura de ITO / PEDOT: PSS / MDMO-PPV / metal, pela técnica de spin coating. É amplamente conhecido que a eletroluminescência destes diodos depende fortemente do material utilizado como cátodo, e também dos parâmetros de crescimento da camada de polímero eletroluminescente MDMO-PPV. **Objetivo.** Neste trabalho o efeito de i) a freqüência do spin coater (1000-8000 rpm), ii) a concentração da solução MDMO-PPV: Tolueno e iii) o material utilizado como cátodo (prata ou alumínio) sobre a resposta elétrica dos dispositivos, foi avaliado por medidas de corrente-voltagem (I-V). **Materiais e métodos.** Películas finas de materiais orgânicos PEDOT: PSS e MDMO-PPV foram depositadas por spin coating sobre substratos de ITO e a estrutura do OLED foi terminada com cátodo de prata e de alumínio. A resposta elétrica dos dispositivos foi avaliada pela sua característica I-V. **Resultados.** Os diodos feitos de películas orgânicas finas fornecem maiores correntes a menores voltagens. Isto pode ser conseguido, quer através do aumento da velocidade de rotação do spin coating ou usando concentrações de MDMO-PPV: Tolueno menores de 2% em peso. Um ajuste dos dados experimentais mostrou que os diodos têm uma contribuição de uma corrente parasita entre anodo e catodo, e outra corrente paralela, onde o principal mecanismo da injeção de portadores da camada orgânica é através da emissão termiônica. **Conclusões.** O ajuste dos dados experimentais, juntamente com a posição dos níveis de energia através da heteroestrutura, mostra que os OLEDs baseados em derivados de PPV são dispositivos unipolares, onde a corrente é atribuída principalmente ao transporte de ocos.

Palavras-chave: semicondutores orgânicos, OLEDs, polímeros eletroluminescentes, MDMO-PPV, PEDOT: PSS, Spin coating, HOMO, LUMO, injeção de portadores, emissão termiônica.

Introduction

Currently the field related with conductive polymers and molecules is widely known as "organic electronics", in opposition to the "traditional" electronics based on silicon and other inorganic semiconductors. A singular advantage of polymers is related with the fabrication process of devices by "wet" techniques such as "spin coating" (1). These techniques are based on the solubility of polymers and therefore are easy to produce, do not require vacuum conditions and remarkably reduce the processing costs. Besides economical reasons, the novel properties of electroluminescent polymers make them attractive for studying new optoelectronic properties of the organic layers themselves, as well as the characteristics of the interfaces that they form with metal and traditional semiconductors. One of the most attractive light emitting p-conjugated polymers for display applications is Poly(p-phenylene vinylene) (PPV) and its derivatives, due to its excellent electroluminescent properties (2). (Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]) (MDMO-PPV) results from a functionalized PPV polymer that improves its solubility in toluene, which enhances the homogeneity of the organic films (3).

Organic semiconductors have attracted many researchers worldwide due to their intrinsic properties. In organic crystals, the molecules and polymers are weakly bonded by Van der Waals forces and hence, the validity of band theory and the subsequent modelling used for describing the optoelectronic properties of traditional semiconductors is often limited. In this paper the mechanism of carrier injection to the organic layer through thermionic emission is discussed. Therefore, it was measured the I-V characteristics of several OLED devices, with several thicknesses of the organic layer prepared by spin coating, and two different types of cathodes." The discussion of the electrical measurements was based on a proposed energy level alignment of the hybrid heterostructure, and a simple model for current injection which allowed a good fit of the experimental data.

Materials and methods

The polymer-based OLEDs fabricated in this work have the structure ITO / PEDOT:PSS / MDMO-PPV / Metal sketched in **Figure 1**. Indium thin oxide (ITO) is a p-type transparent semiconductor in the visible range which is often obtained as a degenerated semiconductor (4). For OLED applications, ITO is used as hole-injecting contact that provides positive charges (anode) to the organic layer MDMO-PPV. Previous studies made by Brütting *et al.* (14) have revealed that thermal conversion of the pre-polymer on ITO substrates leads to a p-type doping of PPV and, additionally, to the formation of an ohmic hole-injecting contact at the ITO/PPV interface.

Electroluminescence is produced in the MDMO-PPV film by recombination of electrons and holes. In order to improve the hole injection, a highly conductive and transparent organic layer of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is used. The transparency of ITO and PEDOT:PSS layers, in the visible range, is a condition needed to avoid absorption of the photons produced in the electroluminescent layer. As a cathode, several metals could be used for injecting electrons to the organic layer, depending on its work function value.

Holes and electrons are injected towards the organic layer from the ITO valence band (E_V) and the metal Fermi level (E_F), respectively. Radiative recombination of electron-hole pairs causes electroluminescence of the device (**Figure 1**). Injection from both electrodes gives rise to bipolar conduction. Assuming a thermionic emission process, the injection barrier for electrons is the energetic difference between the Fermi level of the metal (E_F) and the LUMO (lowest unoccupied molecular orbital) of the electroluminescent layer. If such a barrier becomes high enough (near to 1 eV or larger), electron injection is negligible and the device has unipolar conduction. The barrier for holes (i.e. the energy difference between the valence band of ITO (E_V) and the HOMO (highest occupied molecular orbital) in the electroluminescent layer MDMO-PPV) can be effectively reduced by placing an intermediate energy level (HOMO at the PEDOT:PSS layer), which enhances the probability for hole injection.

The device was fabricated as follows: ITO substrates from the company SPI supplies (R_{sh} ~ 15 to 30 Ω/□), were etched with hydrochloric acid (HCl) by using a plastic mask. As a result, 6 diodes with a rectangular shape of 12 mm^2 area were patterned on each sample. Organic films of PEDOT:PSS and MDMO-PPV were deposited on the ITO substrate by spin coating. Both polymers were supplied by the company Sigma-Aldrich. The PEDOT:PSS solution in water was used as provided by the company, whereas solutions with a weight concentration of 1,8% and 2% of MDMO-PPV in toluene were prepared for the electroluminescent layer. For the polymer deposition, a Laurell WS-400-6NPP-LITE spin coater was used. The spin coating frequency was changed from 1000 rpm to 8000 rpm Vacuum-evaporated

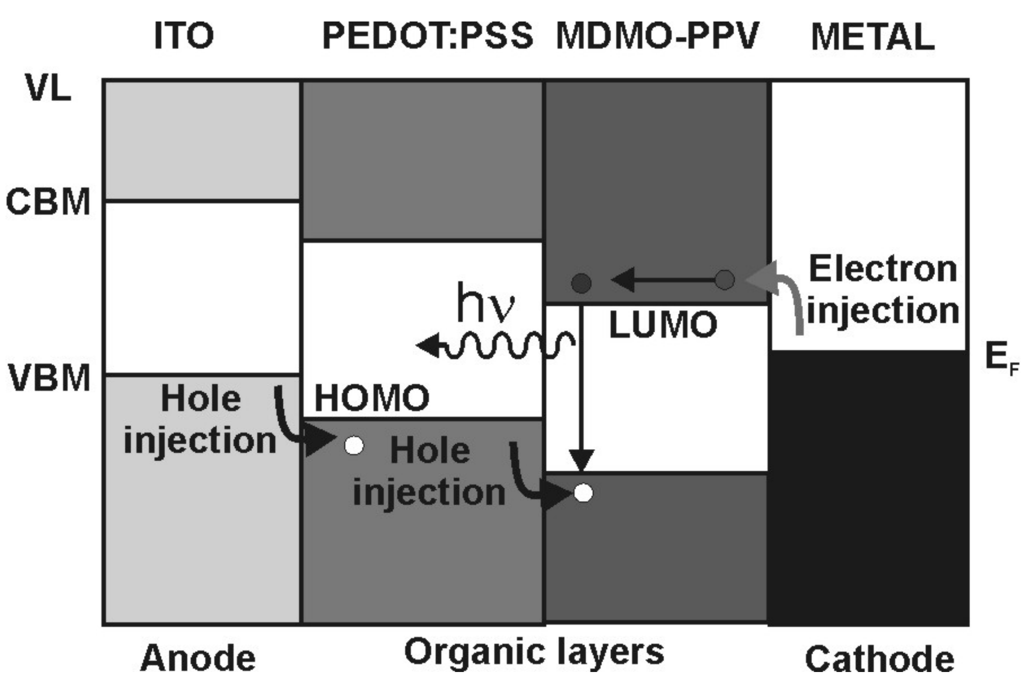

Figure 1. Schematic diagram of a bilayer OLED and its working principle.

aluminium (99,99% Lesker) or silver (99.99% Balzers) were used as cathodes for the devices. Electrical measurements were performed with a Keithley 6220 precision current source, a Keithley 2182 nanovoltmeter and a power supply Array 3631A. All measurement instruments were controlled through GPIB port by an application developed with LabView 8.5, a software for data collection and instrument control.

Results and discussion

Figure 2 shows the I-V characteristics of OLEDs with aluminum cathode. The polymeric MDMO-PPV layer was deposited at several spin coater frequencies. The I-V curves on **Figure 2a** result from OLEDs fabricated with double deposition of the MDMO-PPV layer, whereas OLEDs made with a single electroluminescent layer exhibited the I-V characteristics shown in **Figure 2b**.

In all the samples, an increase in the current intensity is observed when increasing the frequency in the spin coating process. This is related with the thickness of the organic layer, which decreases with an increase in frequency. Higher slopes in the I-V characteristics for devices made with a single organic layer show that these films have a lower overall ohmic resistance, which is probably associated to a higher density of pinholes in thinner organic films. The pinholes provide a path of parasitic currents via direct anode-cathode contact, which contributes with an ohmic component to the net current.

The strong correlation between frequency of the spin coating process and film thickness is confirmed by images of MDMO-PPV films deposited at different revolutions, as shown in figure 3. It can be easily observed that the transparency of the film is enhanced when the frequency of the spin coating process rises, although there is no absolute measurement of the film thickness.

It is widely known that organic materials have low mobilities (5, 14). For MDMO-PPV a field effect mobility of 5×10^{-6} $cm^2V^{-1}s^{-1}$ was measured for spin casted films on a toluene solution (5). Thus, thicker films result in more resistant layers and therefore, lower currents are expected. This observation is confirmed with the higher current intensity measured for devices made with a single layer of MDMO-PPV, compared to those made with a double electroluminescent layer (**Figure 2**). The same trend is observed for OLEDs built with silver cathode as illustrated in **Figure 4.**

Reducing the thickness of the organic electroluminescent layer also decreases the voltage for obtaining electroluminescence. This result suggests that making the electroluminescent layer thinner, the performance of the devices increases, giving rise to an increase in the current intensity

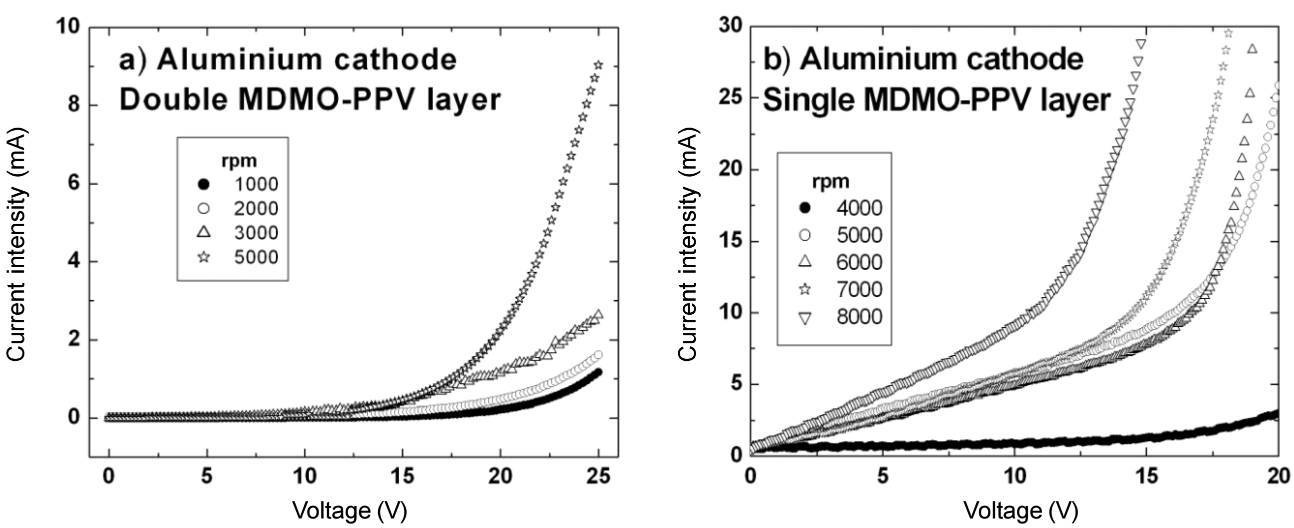

Figure 2. I-V characteristics of OLEDs with aluminum cathode made at different spin coating frequencies with a) double deposition and b) single deposition of MDMO-PPV layer. The polymeric layer was deposited by spin coating, using a 2% weight solution of MDMO-PPV in toluene.

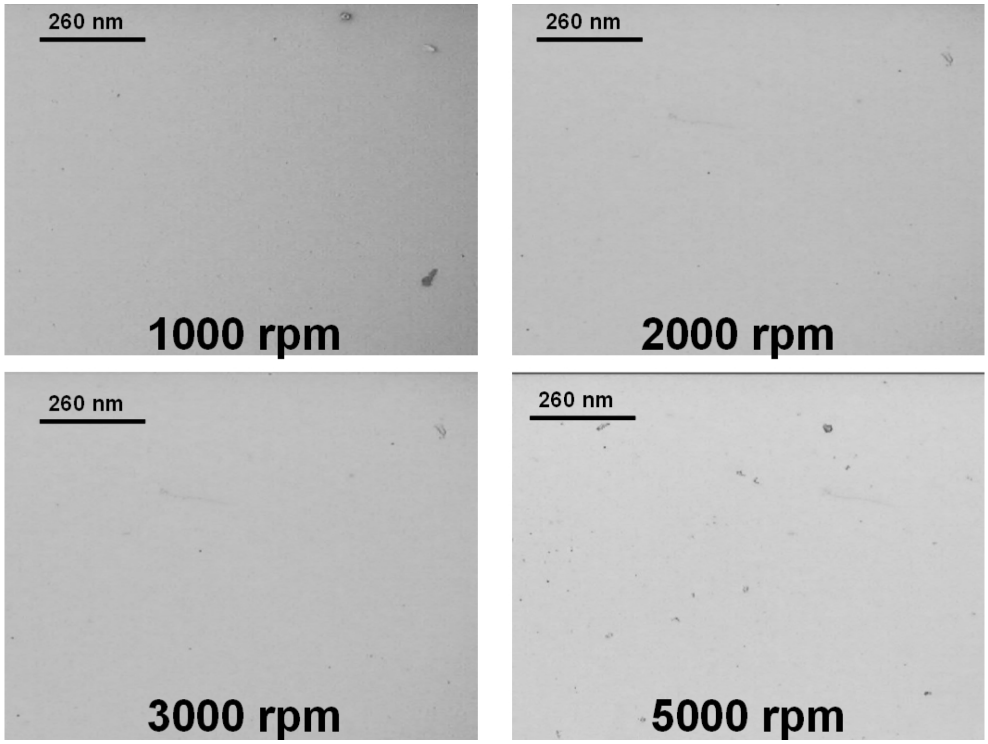

Figure 3. Images of MDMO-PPV thin films deposited at several frequencies by spin coating. In all cases, the concentration of the MDMO-PPV:Toluene solution is 2%.

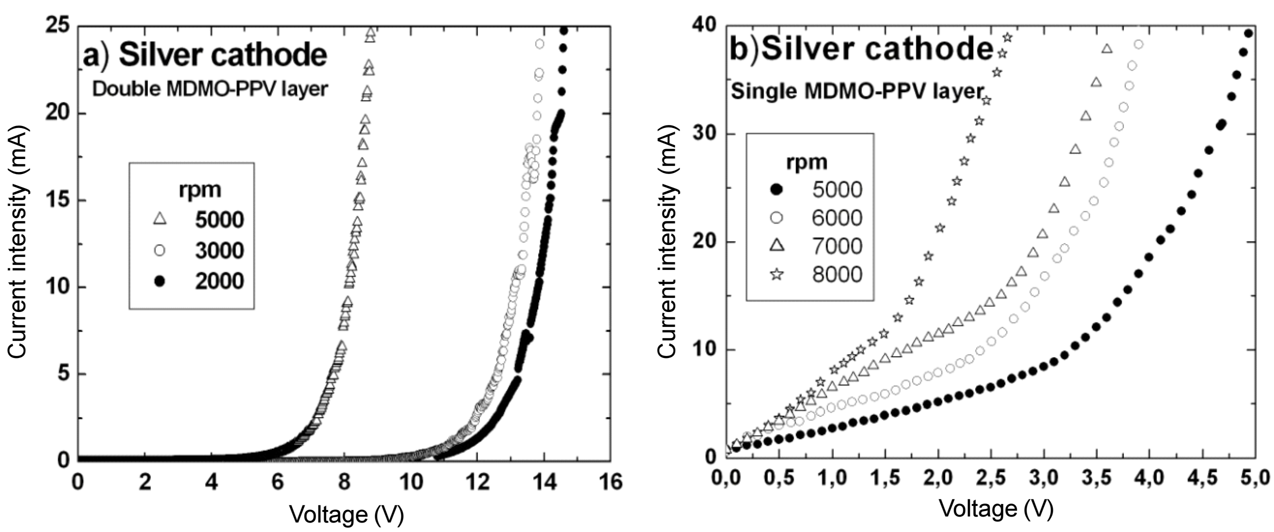

Figure 4. I-V characteristics of OLEDs with Silver cathode made at different spin coating frequencies with a) double deposition and b) single deposition of MDMO-PPV layer. The organic layer was made by spin coating using a 2% weight solution of MDMO-PPV in toluene.

and higher emission intensity. In this way, the increase in the electroluminescence with reducing thickness is due to both an increase in the current intensity by reduction in the effective resistance of the organic layer, and to a reduction in the absorption of the organic layer itself. However, one should be aware that reducing the thickness of the organic layer enhances the probability of having pinholes and thus, parasitic currents and short-circuits between anode and cathode. Another way of reducing the thickness of the organic layer is by decreasing the MDMO-PPV concentration in the solution used for the spin coating process, as shown in figure 5. Two samples with aluminum cathode were prepared with a single layer of MDMO-PPV at 5000 rpm, using MDMO-PPV:Toluene solutions with a weight concentration of 1,8% and 2,0%, respectively. From figure 5, it is clear that a higher current intensity is obtained for devices built with a lower concentration of the solution.

The metal used as cathode strongly modifies the performance of the OLEDs. **Figure 6** shows the I-V characteristics of two devices based on a single electroluminescent layer of MDMO-PPV with the same spin coating parameters (5000 rpm, 2% weight concentration in toluene) and silver and aluminum cathodes, respectively. In general, a better performance of the devices made with silver cathode was observed, since higher currents at lower voltages were obtained

The same result of higher power output for silver cathodes remains true for different frequencies of the spin coater, as evidenced by comparing figures 2a with 4a and 2b with 4b, respectively. For discussing this result, a diagram of the energy level alignment through the whole heterostructure of MDMO-PPV based OLEDs with silver cathode is depicted in figure 7. This diagram considers ITO as a degenerated semiconductor (4, 6) and is based on the reported values of ITO bandgap (7), ITO work function (8), PEDOT:PSS ionization potential (9), PEDOT bandgap (10), MDMO-PPV bandgap (11), MDMO-PPV ionization potential (12), and the work function of silver and aluminum (13).

This diagram assumes a vacuum level alignment; nevertheless dipole formation at organic / inorganic interfaces does affect the energy level alignment and carrier injection. In absence of photoemission measurements or other techniques able to provide an accurate value of energy bands and work functions, figure 7 provides a good starting

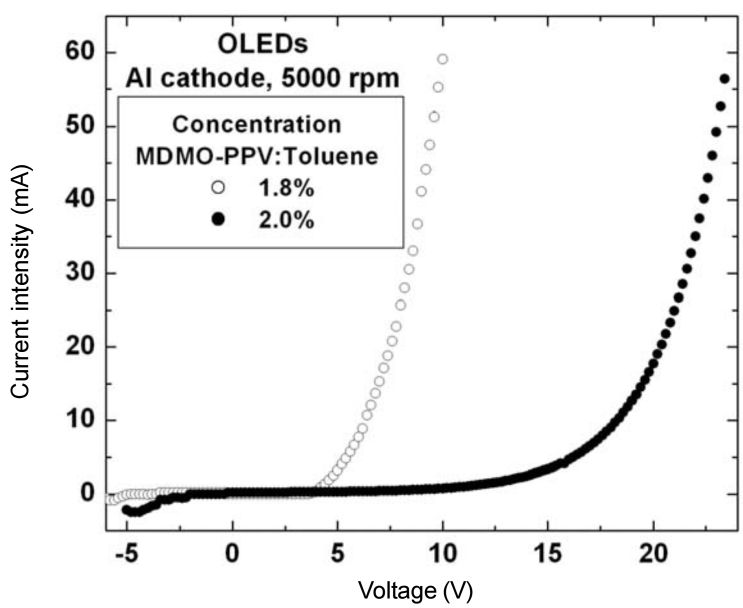

Figure 5. I-V characteristics of OLEDs made with a spin coated single layer of MDMO-PPV at 5000 rpm and aluminum cathode. Two different concentrations (1.8 and 2% weight) of a solution of MDMO-PPV in toluene were prepared for the spin coating process.

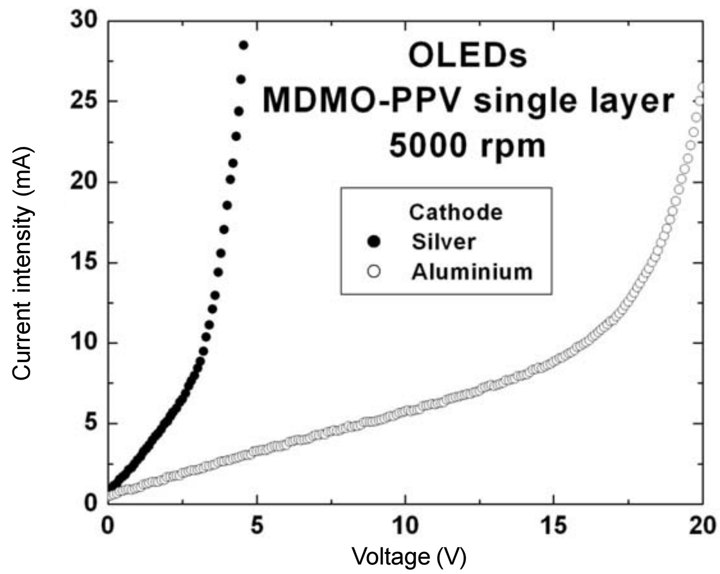

Figure 6. I-V characteristics of two OLEDs made with a spin coated single layer of MDMO-PPV at 5000 rpm, using aluminum and silver cathodes.

point for the discussion of carrier injection mechanisms. According to it, the electron injection barrier for a device with silver cathode is near to 1.7 eV or slightly lower (up to 1.26 eV), depending on their work function value and crystallinity (for polycrystalline silver 4.26 eV and for Ag(111) 4.74 eV), (13).

Taking into account the lower value for the aluminum work function (~ 4.06 eV to 4.26 eV), an electron barrier between 1.06 eV and 1.26 eV is expected, lower than the case of the silver cathode. However, the experimental results shown in figure 5 reveal the opposite: a higher electron injection barrier when aluminum cathodes are used. This fact suggests the oxidization of the aluminum contacts, hence featuring the formation of an additional barrier at the MDMO-PPV / Aluminum interface, which prevents electron injection to the heterostructure.

In general, independently of the metal cathode, the I-V characteristics shows a rectifying behavior, as shown in figure 5, indicating that MDMO-PPV based OLEDs have unipolar conduction mediated by holes. The examination of the energy level alignment (**Figure 7**) shows effective barrier heights for electrons higher than 1 eV, whereas only 0.6 eV of effective barrier height for holes are expected, since there are two consecutive hole injection barriers from ITO to MDMO-PPV.

The injection mechanism in organic interfaces is still a matter of discussion. The most favored mechanisms are thermionic-emission (Richardson-Schottky) or tunnel-assisted injection (Fowler-Nordheim), (14). A fit of the experimental data of a typical I-V characteristics in an OLED with the structure ITO / PEDOT:PSS / MDMO-PPV / Al is shown in **Figure 8**.

In this work, the fit was carried out using a model of a diode in parallel with a resistance. Resistance (2.2 kΩ) represents parasitic currents between the anode and the cathode through pinholes in the heterostructure, which are attributed to inhomogeneities on the organic layers. This contribution is responsible of the linear regime observed at low voltages in the I-V characteristics. The diode simulates transport current through the organic layers. Therefore, the net current has two contributions: the current through the organic diode (i_D) plus parasitic currents (i_Ω) (Equation 1).

$$i = i_D + i_\Omega = i_D + V/R \quad (1)$$

Here, the Richardson-Schottky expression (Equation 2) for the I-V characteristics of a diode i_D was used (15).

$$i_D = i_0 \exp\left(\frac{qV}{nkT}\right) \quad (2)$$

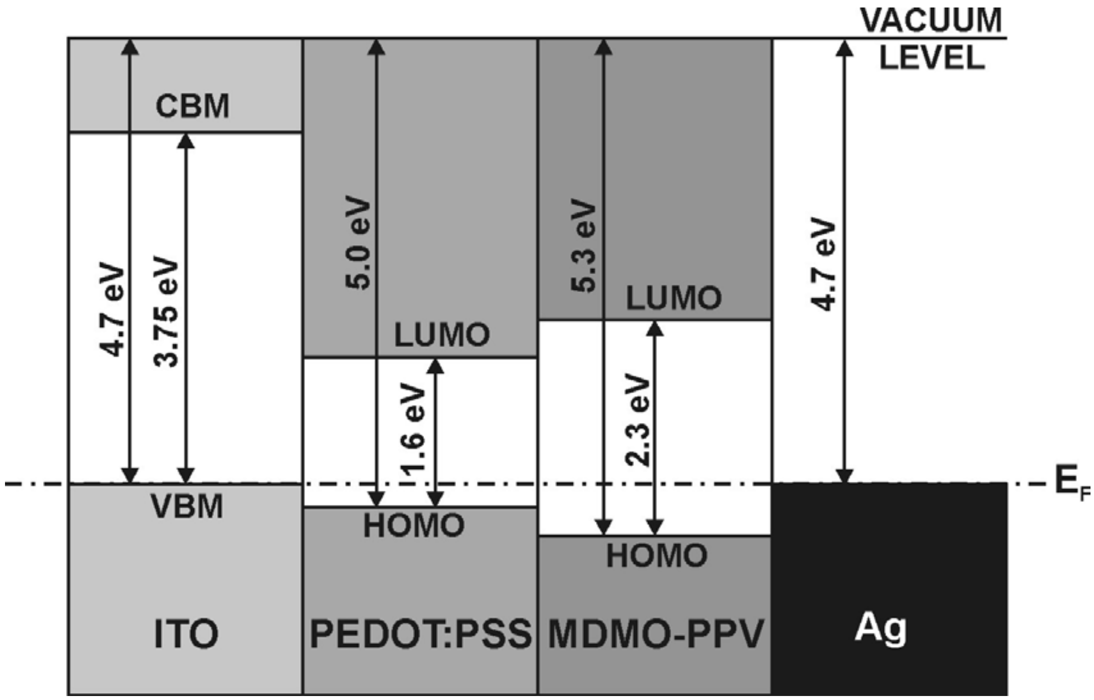

Figure 7. Proposed energy level alignment of the OLED heterostructure ITO / PEDOT:PSS / MDMO-PPV / Silver.

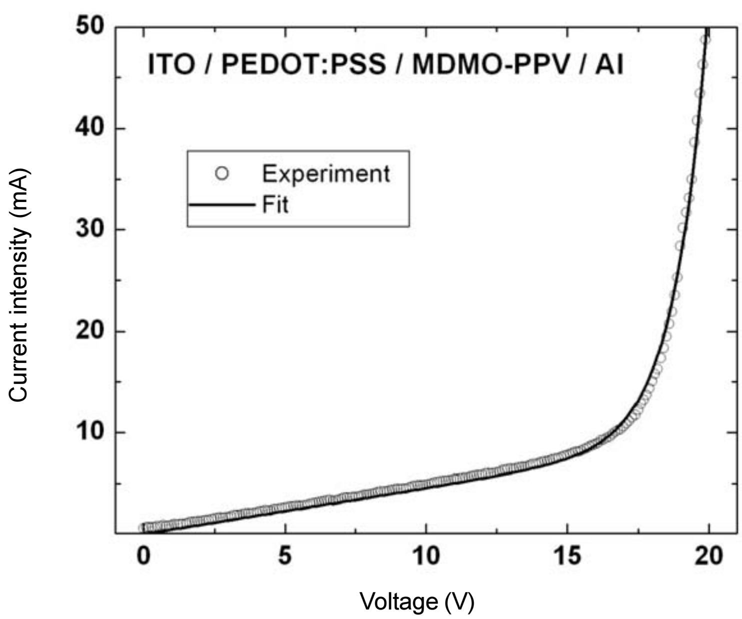

Figure 8. Fit data of typical I-V characteristics measured from OLEDs with aluminum cathode, and a single layer of MDMO-PPV prepared with a 2% weight concentration at 6000 rpm.

Where: q is the elemental charge, k the Boltzmann's constant, T the temperature and n is the ideality factor. The saturation current i_0 is related to the barrier height ϕ_b, the diode area w and the Richardson's constant A^* by means of equation 3:

$$i_0 = A^* T^2 w \exp\left(-\frac{q\phi_b}{kT}\right) \quad (3)$$

The use of the Schottky model for simulating the I-V characteristics of an organic-based light emitting diode suggests that carrier injection is mediated by thermionic emission. However, an estimation of the barrier height using equation 3 is a challenge because the Richardson's constant for organic materials and heterostructures is still unknown.

Conclusions

Polymer-based organic light emitting diodes with heterostructure ITO / PEDOT:PSS / MDMO-PPV / Metal were built by spin coating and the fabrication parameters were evaluated through their I-V characteristics. The results indicate that OLEDs with higher performance in current intensity and light emission are obtained by reducing the thickness of the electroluminescent layer and by using silver as cathode. Reduction in the thickness of the organic layer can be achieved, either by increasing the frequency in the spin coating process or by reduction in the concentration of the MDMO-PPV:Toluene solution. A fit of the experimental data suggests that carrier injection into the organic layer is mediated by thermionic emission. The energy level alignment through the whole heterostructure suggests that conduction in the device is dominated by holes. Additional studies on this topic should be addressed for a more precise assessment of the effective barrier height in MDMO-PPV based OLEDs.

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Conflict of interest

There is no conflict of interest on the type of devices or procedures described in this manuscript.

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