Characteristics of Organic TFTs with PBTTT-C12 as polymeric semiconductor layer

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Abstract. In the fabrication process of OTFTs is necessary to focus on the electrical properties of channel’s materials to improve its behavior and then exploit the use of this technology in different applications. For this reason, this paper was focused into studying the electrical behavior of OTFTs made with PBTTT instead of P3HT OTFT process. Furthermore, two different contacts configuration were also included. The OTFT’s structure used in this work was upper drain and source contacts / top gate contact. In addition, OTFTs output characterizations were measured and their physical-electrical parameters, as mobility and threshold voltage, were extracted by UMEM method. Good agreement in output characteristics was obtained between experimental data and modeled extracted data. Finally, after one month, a degradation of less than 5 % of the output characteristics was observed.

Index Terms. Organic transistor; PBTTT; fabricating process; extracted parameters; output characteristics

I. INTRODUCTION

There are several organic materials that allow us to manufacture devices that are used as sensors for environmental monitoring, the food industry, displays and medical diagnostics [1, 2], having the advantageous characteristics such as: flexibility, transparency, lightness and large area [2]. Organic materials can be classified into those of small molecule (monomers) and those of large molecule (polymers). The advantage of monomers over polymers is their greater mobility to them and comparable to that of amorphous silicon, but their manufacturing requires high vacuum conditions which make the technological process more expensive. On the other hand, the polymers are soluble and thanks to this it is possible to use film-making techniques without vacuum with these materials [3]. However, the mobility of organic materials does not exceed 1 cm²/Vs. It can also be added that organics show high electrical instability. That is why currently an effort is made to study different polymers and their relationship with the mobility parameter. Among the most studied polymeric materials is poly (3-hexylthiophene-2,5-diyl) (P3HT) which achieves a mobility of less than 0.1 cm²/Vs [2, 4, 5, 8]. Other of the polymers studied is poly [2,5-bis (3-tetradeceylthiophen-2-yl) thiene [3, 2-b] thiophene] (PBTTT-C12). Of the works that achieved better mobility, it stands out the one that used stressed films obtained with a long and complex process releasing films and subjecting them to high temperatures, which reached a mobility greater than 1 cm²/Vs [8]. The measured OTFT used a drain voltage of -70 V with a silicon oxide as a gate.

On the other hand, to manufacture a transistor you need contacts, which can have in general the following structures: Top contact, bottom contact and upper contact that have their advantages and disadvantages. Comparing these contact structures, it is observed that the top structure offers us convenience to polarize and measure the devices and the degradation of the polymers is lower in these, but its negative point is a greater resistance. In the case of bottom contact, its benefit is less resistance, but its way of measuring and polarizing becomes complex and there is greater degradation [4 - 6]. In the structure upper contacts add the advantages of the previous structures but their photolithography process is long.

In this article we worked with the PBTTT-C12 dissolved in chloroform used as unstressed semiconductor, the poly (methyl methacrylate) (PMMA) as a dielectric and the upper contacts structure to obtain OTFTs through a simple process. In this way completely organic OTFTs were manufactured, since both the semiconductor and dielectric were polymers. At the same time, a treatment called solvent vapor annealing (SVA) was used to improve the OTFT interfaces and two contact configurations were used (Fig. 1) to compare their effect on electrical measurements [9 - 11]. It was possible to obtain a mobility of $2.17 \times 10^{-3}$ cm²/Vs with a source-drain polarization of -30 V. And a change of less than 5 % was obtained between the output characteristics of the OTFT measured after its manufacture and those obtained one month later.

II. FABRICATION PROCESS

OTFT manufacturing process described in [7] was followed in this work as it was mentioned previously; however, an extra treatment (vapor solvent annealing) was added in order to improve the device interfaces [12-14], especially in active film as in [9 – 11]. In addition, all the fabrication process was prepared in N₂-filled glovebox. Fabricated OTFTs are showed in Fig. 2, where it is possible to see the transversal view of structures.

The device fabrication process consisted on the following steps:

A. Drain and Source patterns

Chromium and gold thick layer of 100 nm and 10 nm were deposited over glass by electron beam. Then, a
photolithography process was done to pattern drain and source contacts (fig3-a). Next, a solvent vapor annealing (SVA) was used with ortho dichlorobenzene (ODCB) (CAS: 95-50-1) during 15 minutes; in this step, the samples were placed inside a petri box and covered to avoid light exposition. Finally, the samples were dried during 10 minutes under vacuum atmosphere in order to prepare the contacts surface for the next film deposition.

B. Semiconductor layer

Firstly, PBTTT-C12 (CAS: 888491-18-7) was dissolved in chloroform (CAS: 67-66-3) with a concentration of 6.53 mg/mL. Then, the polymeric solution was heated at 45 °C and stirred for 140 hours. Later, the solution was filtered with a 0.2 µm syringe filter before being deposited by spin-coating. The spin-coating conditions were: 300 rpm during 30 seconds subsequently 1000 rpm for 30 seconds to get 40 nm of layer thickness (Fig. 3-b). A (SVA) with ODCB was made to the films again for 10 minutes. Subsequently, the samples were dried for 10 minutes under vacuum, and the films were also annealed at 130 °C on a hot plate for 20 minutes. Afterwards, another SVA was made with 1 mL of anisole for 3 minutes.

C. Insulator layer

A solution of poly(methyl methacrylate) (PMMA) dissolved in anisole, purchased from Sigma-Aldrich®, was filtered by 0.45 µm syringe filter, then deposited by spin-coating at 5000 rpm during 45 seconds to get a 440 nm layer thickness (Fig. 3-b). Next, the samples were dried for 15 minutes under vacuum, and the films were annealed at 90 °C on a hot plate for 20 minutes. Finally, SVA was made with 1 mL of anisole during 3 minutes and then dried for all night in vacuum.

D. Top contacts

At first, a reactive ion etching (RIE) process was accomplished to open windows across the polymeric layers to make contact with buried patterns (drain and source) with the help of a dry O₂ atmosphere for 12 minutes (Fig. 3-c). Next, a second sputtered gold layer of 80 nm was deposited. Finally, the upper contacts were patterned by photolithography process (Fig. 3-d).

III. RESULTS AND DISCUSSION

The energy gap (Eg) of PBTTT-C12 films was determined by absorption spectroscopy (UV-vis), which was carried out through the V670 Spectrophotometer. As a result, the calculated Eg of the films was 1.75 eV, where the Tauc method was used. This result differs from others previously reported [1,16] to the same polymer, which Eg were in a range from 1.91 to 1.93 eV, where the dissolvent was used was dichlorobenzene. This can happen due to solution crystallinity [9]. For this reason, it is possible to suppose the CHCl₃ achieve a different value of crystallinity compared to ODCB.

Subsequently, the transfer and output characteristics were measured in order to compare the electrical performance of OTFTs fabricated in this work with PMMA-P3HT [7] and PBTTT dissolved in ODCB [2]. To achieve this, several OTFTs were fabricated and measured varying the channel length (L) and width (W) (figure 4), some of them were showed and presented in this work marked as: C1T3 type with W = 110 µm and L = 30 µm presented configuration 1, C2T4 type W = 500 µm and L = 10 µm and C2T8 type W = 210 µm and L = 20 µm presented configuration 2. Room-temperature current-voltage (I-V) characterization was done through a Keithley Test System 236 Source Measure Unit and Signatone Probe Station S-1160 under a nitrogen flow.

Drain current density was calculated based on measured output characteristics with gate voltage steps of -10 V from 0 to -40 V under a sweep drain voltage from 0 to -30 V and a source voltage at 0 V for C1T3 and C2T4 (Fig. 5 and 6). Both OTFT's showed an intrinsic conductivity at VG = 0 V due to semiconductor polymer as in the case of P3HT [7].
Also, in C2T4 is observed a nonlinear behavior and unsaturated drain current at high gate voltage, which indicates a high contact resistance like in [16] because of the overlap in C2 was bigger than C1.

Figure 6 shows the output characteristics of C2T8 immediately fabricated, and after one month fabrication was plotted too. As it is appreciated, current density variation after one month was less than 5%, which results a density current degradation much lower than reported in [7]. According to this result, it is possible to prove that PBTTT-C12 semiconductor presents a more stable electric performance than P3HT as it is previously mentioned.

A comparison of OTFT’s electric performance between the ones presented in this work and the ones reported in [2] is showed in table I. A similar value of density current was obtained with OTFTs C1 (this work) compared with [7], where P3HT was used in the same fabrication process instead of PBTTT-C12. However, if we consider the other configuration used in this work (C2), it is possible to observe an increment in the density current at high gate voltage, which indicates a high contact resistance like in [16] because of the overlap in C2 was bigger than C1.

Figure 7 shows the output characteristics of C2T8 immediately fabricated, and after one month fabrication was plotted too. As it is appreciated, current density variation after one month was less than 5%, which results a density current degradation much lower than reported in [7]. According to this result, it is possible to prove that PBTTT-C12 semiconductor presents a more stable electric performance than P3HT as it is previously mentioned.

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In addition, the positive threshold voltage ensures the intrinsic conductivity in all OTFTs. In figure C1T3 shows the lowest value for "interD", which indicates almost no influence of non-ohmic contact due to this parameter involved in diode resistance ($R_{co}$) from equation 3. Parameter $R$ is calculated through four resistances: a) the slope in linear region from I-V output, b) the mobility, capacitance and W/L are involved, c) the metal resistance and d) the diode resistance.

$$R_{co} = \frac{\eta kT}{q \log\left(\frac{I_{DS}}{10 \text{interD}}\right) I_{DS}} \quad (3)$$

Where $\eta$ is the ideality factor of diode and interD is the intercept of the curve log($I_{DS}$) vs $V_{DS}$

The output characteristics measured and modeled with extracted parameters of transistors C1T3, C2T4 and C2T8 are showed respectively in Fig. 8 - 10, with good congruence. However, it is well known that OTFTs can present deformation at the origin of the output characteristics, due to non-ohmic contacts at drain and source [17]. It is observed in C1T3 an almost ohmic contacts, meanwhile in C2T4 and C2T8 presents a non-ohmic contacts, which was possible to model by varying the value of "interD" parameter. The results for modeled curves corresponding to $V_G = -10 \text{ V}$ and $-20 \text{ V}$ showed a variation between measured and modeled curves.

### IV. CONCLUSIONS

In this work it was shown that it is possible to obtain fully organic OTFTs with PBTTT-C12, dissolved with chloroform as an active film using a simple technological process in addition to the SVA treatment. A mobility of $2.17 \times 10^{-3} \text{ cm}^2/\text{Vs}$ was achieved without thermally stressing the active film with a $V_d = -30 \text{ V}$ and a channel length of 30 $\mu$m.
It was also possible to observe a change of less than 5% in the output characteristics in C2T8, between measurements made with a space of one month. From the results between configurations C1 and C2, it is suggested that C1 is the best option to perform the contact patterns to avoid the increase in resistance in the contacts, and it is speculated due to the overlap of the gate area on the drain contacts. and source. This provides an excellent option of OTFT where is required to perform the contact patterns to avoid the increase in resistance in one organic field-effect transistor.

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