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Photodetector behaviour in polyfluorene-based Polymer Light Emitting Diodes (PLEDs)

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Polymeric light emitting diodes (PLEDs) as potential light detector devices, have been studied. Two different polymers: one commercially available *Poly(9,9-dihexilfluorene)* (PFC_6) and other one -synthesized specially for optoelectronic applications- *Poly(9,9-bis(6'-brominehexil)-fluorene phenylene)* ($PFBr_2$), have been used as active layer for the diodes. A significant improvement of the photocurrent is observed in the new synthesized polymer by comparison with the commercial one. Diodes made with $PFBr_2$ show a linear dependence of the photocurrent generation on the incident light power, but the stability of the photocurrent for different bias encountered in these diodes is not as good as the typical level found in inorganic ones.

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1. Introduction

Since the first successful demonstration of polymer light emitting diodes (PLEDs) [1-3] from a conjugated polymer in 1990, PLEDs have attracted worldwide attention as candidates for the next generation of emissive flat panel displays, and the same organic structures have been used as light detector devices, like photodiodes or solar cells [4-7].

The wide experience reached in the development of inorganic semiconductor based optoelectronics has allowed a fast progress in this field. Furthermore, the advantages shown by these polymer LEDs in contrast to inorganic ones rest on the ability of depositing thin polymer films using low cost methods like spin-coating, ink-jet printing, etc. on practically any type of substrate, even flexible ones [8], and allowing the tuning of the emission colour over the full visible spectrum. The techniques mentioned above, that do not require such complex equipments like those based in ultra high vacuum systems, have clearly contributed to increase the interest and the number of investigations in this field.

Polyfluorene-based polymers have attracted attention as a blue emitting material for PLEDs. Polyfluorene offers a high fluorescence quantum yield along with good chemical and thermal stability. Cambridge display technology reported efficient blue-emitting devices with polyfluorene polymers [9]. However, polyfluorene-based PLEDs provide insufficient blue-color chromaticity. This is why a full colour display of PLEDs shows yellow-tinged colour [10-12]. Light emitting diodes have been the widely studied devices, but nowadays the interest is being distributed into other devices like photodetectors and solar cells [13-16].

In this work we study the photocurrent generation properties presented by polyfluorene-based diodes which were at first designed as light emitters.

2. Experimental

2.1. Devices fabrication

Devices studied in this paper were fabricated using spin-coating technique, with the exception of the final electrode, that was deposited in a high vacuum chamber.

The fabrication process started with a polished glass substrate coated with a thin (100 nm) semitransparent indium-tin oxide (ITO) layer with a resistivity of 60 ohms cm, which will act as the anode of the devices. These substrates were put under a cleaning procedure, consisting in dipping the substrates in a NaOH 10% aqueous solution for three minutes at a temperature of 55 ºC. Then, they were rinsed with abundant deionized water for one minute approximately.

A hole-injecting layer -PEDOT:PSS (Aldrich grade electronic application)- was spin-coated at a spin rate of 6000 r.p.m. from its water solution (1.3 wt%) onto the ITO substrate, and then cured at 80 ºC for an hour in order to enhance the evaporation of the solvents. PEDOT thickness was around 75 nm. Using the same technique, a layer of the non-commercially available copolymer (identified like $PFBr_2$), was spin-coated from its tetrahydrofuran solution (20 mg/ml) at 4000 r.p.m. during 30 seconds.

Finally, an aluminium cathode was vacuum-deposited through mask using Joule effect method.

The structure described above matches the sample labelled as A. In order to compare, equivalent diodes were

fabricated using an active layer of commercial fluorene homopolymer (PFC_6). This polymer was also purchased from Aldrich. These devices with the structure (glass/ ITO / PEDOT:PSS / PFC_6 /Al), were labelled as B. The deposition conditions of the PEDOT:PSS layer and the PFC_6 active layer in sample B were totally analogous to those of sample A.

Fig. 1 shows the chemical structure of the polymer used as active layer in each sample.

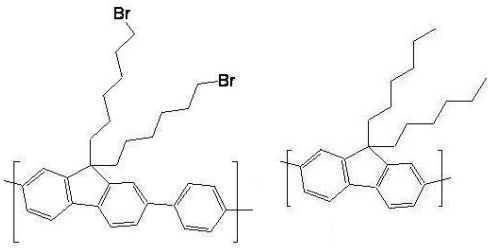

Fig. 1. (a) Chemical structure of the $PFBr_2$ polymer used as active layer for A-type diodes. (b) Chemical structure of the PFC_6 polymer used as active layer for B-type diodes.

2.2. Theoretical principles

There is nearly no essential difference between the basic structure of a solar cell and a photodiode. The only difference relies on the type of application. Photodiodes are required to have maximum linearity and minimum response time and noise, while solar cells are meant to give maximum energy and efficiency.

The photovoltaic effect takes place in both solar cells and photodiodes, when the built-in potential barrier formed between p-type and n-type layer is illuminated. Fig. 2 shows the band profile of a p-n junction under illumination.

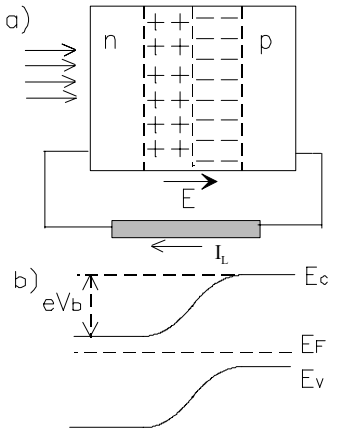

Fig. 2. a) Scheme b) band diagram of the p-n junction under illumination.

In absence of illumination, and as a result of a diffusion process of the majority carriers (holes from p-type layer to n-type layer and electrons from n-type to p-type layer), it will appear due to violent recombination, a depletion region at the physical junction of the two types of semiconductors. This space charge sets up an electrostatic field which opposes further diffusion across the junction in the built in electrostatic field. Equilibrium is established when the diffusion of majority carriers across the junction is balanced by the drift of minority carriers back across the junction in the built in electrostatic field. This thermal equilibrium is broken when the p-n junction is illuminated with a radiation of energy greater than the energy of the band gap of the semiconductor. The existence of a potential barrier that favours the movement of the minority charges makes those minority charges that reach the barrier be drifted by the field at the depletion region, and will generate a current I_L at the external circuit (or a electronic potential difference if the device is at open circuit).

Under illumination, the diode will be equivalent to a current generator of value I_L (that will depend of the incident light flux and the device's parameters) in parallel with an asymmetric, non linear resistive element, i.e., a diode. If in conditions of darkness the characteristic I(V) of the diode is:

$$I(V) = I_s[Exp(eV/KT) - 1] \tag{1}$$

Under illumination it will be:

$$I(V) = I_s[Exp(eV/KT) - 1] - I_L \tag{2}$$

The short circuit intensity will be defined as:

$$I_{CC} = I(V = 0) = -I_L \tag{3}$$

And the open circuit potential as:

$$V_{CA} = V(I = 0) = \frac{kT}{e}\ln\left(\frac{I_L}{I_s} + 1\right) \tag{4}$$

I_{CC} intensity will be, in general, proportional to incident light flux and will depend on the surface of the diode and its spectral response. In order to get lineal response, reverse bias must be assumed. In these conditions, the generated reverse current will be neglected versus photocurrent.

The same theoretical working principles of inorganic semiconductor based devices are applied to organic based ones, being widely accepted a parallel "energy bands – type" theory for organic semiconductors in which the valence and conduction band are transformed in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

2.3. Procedure

The current-voltage (I-V) characteristic curves of these diodes working as photodiodes were measured under different illumination conditions as their principal characterization. A common 100 W white light bulb was used as spotlight, whose intensity was regulated by a Triac BT139 from Philips. The power-meter of the mentioned spotlight was a Spectra-Physics (model 470A) instrument. In order to characterize I-V curves for different incident power light we employed a Keithley 2400 Sourcemeter instrument controlled through the IEEE-488 interface. A LabVIEW (National Instruments) program was performed to use pulsed voltage signal in order to avoid the degradation of the devices due to heat. Thus, the duty cycle of the waveform could be controlled, as well as the start and the end point of the sweep. Moreover the number of measure points could be set, i.e., the step of the sweep.

First of all, a study of the influence of down time of the waveform was carried out, finding that it was not relevant to get the characterization curves. This way, one second for down-time (t_B) and seven milliseconds for up-time (t_H) were adopted to avoid degradation effects, being the duty cycle of the 0.7 % for all I-V curves presented in this paper. Fig. 3 shows the generic form of the mentioned pulsed waveform.

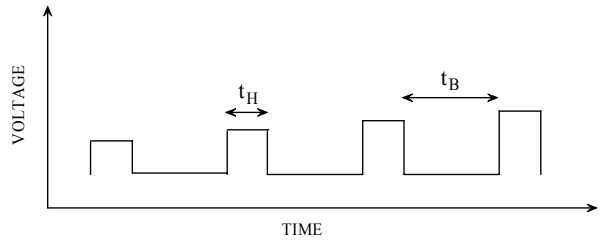

Fig. 3. Waveform of the Keithley 2400 Sourcemeter programmed pulse employed in the electronic characterization (I-V) of the polymeric diodes (not on scale).

3. Results and discussion

I-V curves for two different polymeric samples are presented: A, employing as active layer the $PFBr_2$ polymer -synthesized for optoelectronics applications- and B, using commercial polymer PFC_6. Furthermore, sample A results for two diodes with different diameter are presented to study the effect of the size of the diodes in the photocurrent, keeping the same bias. All the performed diodes have circular shape. The diode labelled as A_1 at A sample has a diameter of 2.0 mm while labelled as A_2 has 2.5 mm.

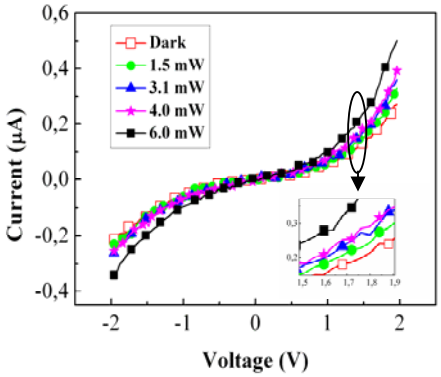

Fig. 4. Current versus voltage curves for A_1 diode (2mm) -using $PFBr_2$ as active layer- for different incident-Light power. The inset is a zoom-in of the graphic where the light effect is appreciated for each I-V curve.

At graphics of A_1 (fig. 4) and A_2 (fig.5) I-V curves of the diodes, positive voltage means reverse bias, while negative means direct bias.

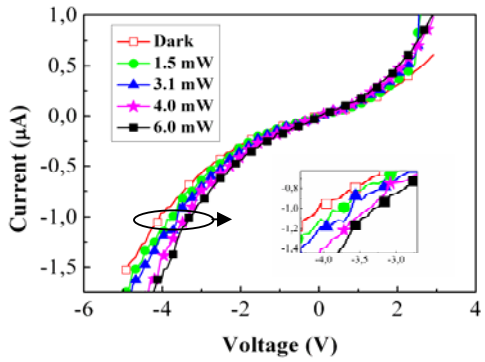

Fig. 5. Current versus voltage curves for A_2 diode (2.5 mm) -using $PFBr_2$ as active layer- for a different incident-Light power. The inset is a zoom-in of the graphic where the light effect is appreciated in each I-V curve.

Analyzing experimental data at I-V curves from Figs. 4 and 5, it can be concluded that the size of the diodes is hardly relevant for the photocurrent. For instance, for I-V curves of the A_1 diode in figure 4, -in darkness conditions and a reverse bias of 2 Volts- a 0.3 μA current is observed. The same value of current is found for the A_2 diode in figure 5 with the same mentioned light conditions and bias. Likewise, for the largest value (6 mW) of the illumination power range and keeping constant the bias – reverse bias of 2 Volts-, the photocurrent for both A_1 (2 mm) and A_2 (2.5 mm) diodes is 0.5 μA.

The results obtained for a positive bias of 2 Volts are very similar. In darkness conditions, a current of 0.2 μA is crossing A_1 diode, whereas for the A_2 diode the current

has a value of 0.3 μA in the same light conditions. Maintaining constant a positive bias of 2 V and incident light power of 6 mW, a current of 0.3 μA and 0.4 μA are crossing A_1 and A_2 diodes respectively.

According to these results we find that the size of the diodes is hardly relevant for the photocurrent or, at least, it is not significant until the tenth of μA.

Fig. 6 verifies that certain linearity exists between incident light power and the current across the diodes. Concretely, a linear regression curve was calculated, finding for A_2 diode with a reverse bias of 0.4 V a slope value, i.e., a sensibility value in μA/W of (6 ± 1) with a correlative coefficient of 0.98.

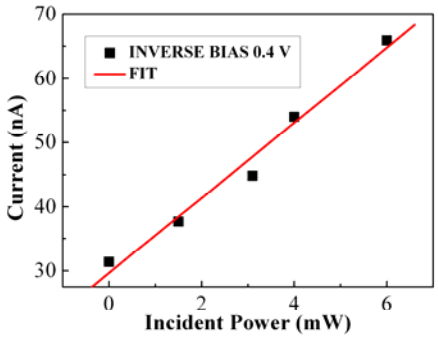

Fig. 6. Current versus incident light power for A_2 diode (2.5 mm of diameter) with reverse bias of 0.4 V.

Similar results were obtained for A_1 diode with reverse bias of 1 V. Concretely, current-incident light power sensibility was (8 ± 2) μA/W with a correlation coefficient of 0.93. Furthermore, the greater bias voltage the greater sensibility is verified. Particularly, increasing the bias voltage from 0.4 to 1.0 Volt, makes the sensibility increase 2 μA/W.

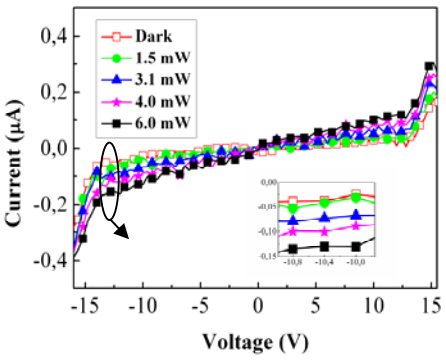

Fig. 7. Current versus voltage curves for B_1 diode (2 mm) -using PFC_6 as active layer- for a different incident-Light power. The inset is a zoom-in of the graphic where the light effect is appreciated in each I-V curve.

Fig. 7 shows the results obtained for the diode labelled as 1 related to the sample B which uses as active layer the PFC_6 polymer -commercially available- and has the same diameter (2.0 mm) as the diode 1 of the sample A.

Relevant differences have been encountered between commercial (Fig. 4) and non-commercial (Fig. 7) polymers. The driving voltage for the devices that use the synthesized polymer is around 2 volts while for the commercially available is around 15 volts. This means that less bias voltage is needed to reach the same level of current for the non-commercial polymer. Particularly, with 6 mW of incident light and a reverse bias of 2 V, current across diode at sample B is 0.03 μA versus 0.50 μA across diode 1 at sample A.

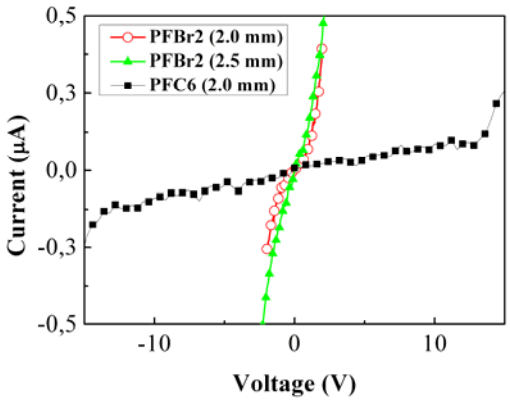

Fig. 8. Current versus voltage curves for A_1 diode –(2.0 mm) and $PFBr_2$ as active layer- , A_2 diode –(2.5 mm) and $PFBr_2$ as active layer- and B_1 diode –(2.0 mm) and PFC_6 as active layer-, all for a 4 mW incident-Light power.

Fig. 8 summarises these results by putting together three different current-voltage curves from figures 4, 5 and 7. Each one corresponding to diodes A_1, A_2 -using the polymer $PFBr_2$ specially synthesized for optoelectronic applications- and B_2 -using the commercially available polymer PFC_6- for an incident light power of 4 mW. It can clearly be appreciated the great difference in photocurrent existing between the diodes fabricated with $PFBr_2$ and PFC_6. This implies a much better performance for those devices using as active layer the non commercially available polymer.

From theory exposed in equations (1) to (4) we might expect I-V curves were vertically displaced for different power radiation. This is not observed at figures 4, 5 and 7, which is normal for organic devices [7]. The reason for this could be a more pronounced superposed resistive behaviour in organic devices that masks the effect of the photocurrent, due to the mechanisms that make difficult the injection of carriers in polymeric devices.

Although it has not been presented here, a lineal behaviour of the photocurrent as a function of the incident light power was registered for experimental data concern-

ing B_1 diode. However, this diode showed a lower sensibility than the diodes fabricated with $PFBr_2$ for the same light conditions and bias. In particular, a sensibility value of (4 ± 1) μA/W and a correlation coefficient of 0.95 have been found from the linear fit carried out to B_1 diode for a reverse bias of 0.4 V.

4. Conclusions

The possibility of using PLEDs fabricated with the commercial polymer PFC_6 as photodetectors presents disadvantages versus those fabricated with the new polymer synthesized at the "instituto de Biología Molecular" of our university, $PFBr_2$.

One of the reasons is the worse efficiency as photodiodes of the first ones, being the photocurrent at approximately a lesser magnitude order for the same incident light and bias conditions.

Furthermore, a good linearity has been found between the level of the photocurrent and the incident light power for both polymers, although diodes fabricated with the $PFBr_2$ polymer present a greater sensibility (μA/W).

For the polymer specially synthesized for optoelectronic applications it has been concluded that the size of the diodes is hardly relevant for the photocurrent or, at least, it is not significant until the tenth of μA.

In summary, although the behaviour can be improved, fabricated polymeric LEDs might be used as photodetectors as well as light emitters. Nevertheless, the stability of the photocurrent for different bias encountered in these diodes is not as good as the typical level found in inorganic ones.

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