VISIBLE AND INFRARED LIGHT PULSE DETECTION WITH ORGANIC SEMICONDUCTORS

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ABSTRACT

Organic semiconductors can act as active material in light pulse detectors. In this paper we highlight the principal features of organic photodetectors (OPD) and we summarize results obtained by different prototype realizations in the visible and near-infrared (NIR) range of the spectrum. Furthermore, we demonstrate that it's possible to change their spectral absorption by means of reduction or oxidation of the molecule in order to realize photodetectors whose responsivity matches three optical fiber windows.

1. INTRODUCTION

Devices based on organic semiconductors are attracting for optoelectronic applications because of a set of very appealing properties, among which the luminescence in the visible and very high absorption coefficients. Photodetection with organic materials is a difficult task: photon absorption by a molecule leads to the formation of an electron-hole bounded state, namely exciton, which has to be dissociated in order to obtain free carriers. Furthermore, carrier transport occurs by intermolecular hopping, thus affecting mobility [1]. Nevertheless, mechanical properties and low cost processability justify efforts made towards organic photodetection. Exciton dissociation can be assisted by an external electric field applied. Some groups improved exciton dissociation by the realization of donor-acceptor interfaces; when excitons reach these interfaces by diffusion, the difference between energetic levels of donor and acceptor induces electron(hole)-transfer, thus generating free carriers. Efficient devices were obtained in the visible range of the spectrum by alternating donor and acceptor in a multilayer stack [2][3] or blending them to form a bulk heterojunction [4].

We concentrated our efforts in realizing photodetectors whose responsivity is matched not only to the visible range of the spectrum, but also to the NIR range, more interesting for telecommunications. Realization of detectors in the NIR range is usually limited by the poor thermal and chemical stability of organic materials with low HOMO-LUMO energy gaps[5]. In spite of this, two classes of coordination metal complexes with organic ligands (transition metal dithiolenes and ruthenium dioxolenes) show strong NIR absorption with a good thermal and chemical stability. In this paper, we demonstrate that their energy gap can be tuned by changing the oxidation state in order to realize photodetectors whose spectral responsivity matches optical fiber communication windows. We tested the capability of these devices in detecting trains of both visible and NIR light pulses.

2. DEVICE STRUCTURE

Our prototype photodetectors are fabricated on a 500μm thick quartz substrate with pre-lithographed metal contacts, the distance between electrodes being 3, 6 or 12μm. Active material is simply deposited on this planar structure, as shown in Fig. 1. Responsivities are measured by illuminating the device with a set of light emitting diodes and biasing it with a voltage source; photocurrents are measured connecting the device to a transimpedance amplifier.

We chose a planar Metal-Semiconductor-Metal structure instead of a vertical one to lower the capacitance, thus improving signal-to-noise ratio, to avoid metal evaporation on the semiconductor, that can damage it, and to remove the requirement of a transparent contact, thus making easier the choice of metal contacts to reduce dark currents.

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3. RESULTS AND DISCUSSION

In this section we report on prototype photodetectors based on organic semiconductors with spectral responsivity matched to visible radiation and to optical fiber windows. For every single spectral range we chose an organic active material with appropriate absorption peak, we deposited it on the planar substrate, we measured external quantum efficiency (EQE) and we acquired time response to a train of light pulses.

3.1 Visible light organic photodetectors

It's easy to find stable organic semiconductors with absorption peak in the visible range of the spectrum. One of these materials is P3HT (poly-3-hexylthiophene), which exhibits strong absorption at approximately 500nm. P3HT shows very good stability and high hole mobility [6]. Furthermore, when it's deposited on a functionalized substrate, surface carrier mobility is enhanced. In order to exploit this feature, we didn't blend P3HT to other materials. By depositing P3HT from solution of chloroform on our substrate, functionalized by dimethyl-dichlorosilane, we obtained a photodetector whose responsivity is matched to about 500nm and reaches an external quantum efficiency of 0.5%, as we can see in Fig. 1. In the same figure is reported the time response to a train of light pulses at a repetition rate of 4Mbit/sec.

3.2 Photodetectors spectrally matched to the first optical fiber window

In order to obtain detectors spectrally matched to the first optical fiber window, we chose as active material complexes belonging to the general class of neutral $[M(R,R'timdt)_2]$ dithiolenes (M=Ni,Pd,Pt; R,R'timdt=monoanion of disubstituted imidazolidine-2,4,5-trithione) [7,8], which show a very intense absorption at 1000nm in chloroform solution (Fig. 2, left). In solid state absorption spectra, the peak is broader and blue shifted, thus matching the first window. In spite of their low energy gap, dithiolenes show good thermal and chemical stability. The dithiolene based photodetector has an enhanced efficiency in correspondence of the absorption peak, as expected, thus reaching a value of about $0.1*10^{-2}$% (Fig. 2, right). Lower efficiency in respect of P3HT based device is probably due to lower carrier mobility. Time response to a train of light pulses at a repetition rate of 200 Kbit/sec was measured.

3.3 Photodetectors spectrally matched to the second and third optical fiber windows

By means of chemical tailoring, it's possible to modify the optical energy gap of molecules. For example, by introducing a negative charge in the molecular framework of a neutral dithiolene, the absorption peak shifts to lower energies, up to match the third optical fiber window (Fig. 2, left) [9]. Similarly, another complex, the dinuclear ruthenium-dioxolene, shows an absorption spectra depending on the oxidation state [10]; in the +3 state it has a particularly intense absorption maximum in the second window. In both cases, solid state absorption spectra reflect this change due to chemical reduction and oxidation. Photodetectors based on these materials were realized by depositing them on the planar substrate described in section 2.

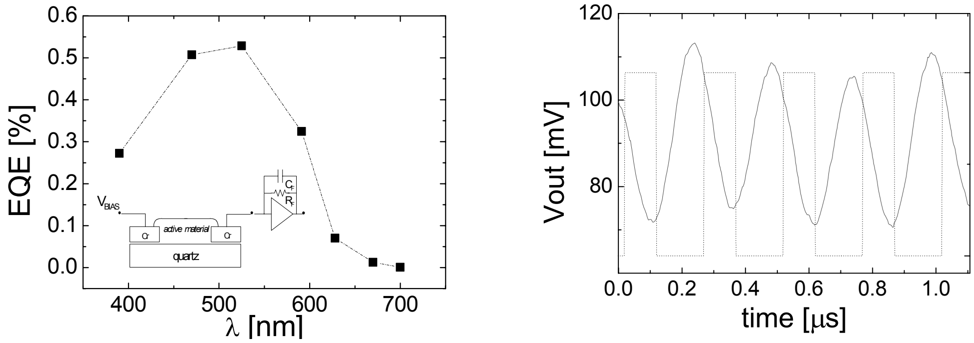

Fig. 1. On the left side, EQE of P3HT based device. P3HT was deposited on a substrate with interdigitated Cr and Au contacts spaced 6μm and presenting an effective width of 15mm (Vbias=-40V). The inset shows a schematic representation of the planar configuration adopted for the photodetector, biased and connected to a transimpedance amplifier. On the right side, time response to a train of light pulses (dotted lines) of 100ns at a repetition rate of 4MHz, performed by connecting a band pass filter to the transimpedance amplifier; this generates a time lag between the light pulse and the photocurrent.

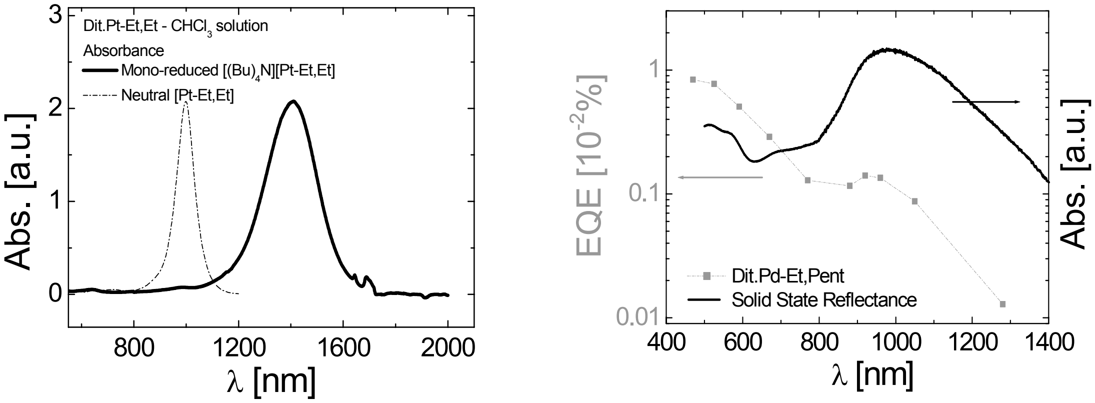

Fig. 2. On the left side, normalized UV-Vis-NIR spectra of [Pt(Et,Et timdt)$_2$] (dotted line) in $CHCl_3$ and of [Pt(Et,Et timdt)$_2$]$^-$ (continuous line) in CH_2Cl_2. On the right side, the diffuse reflectance spectrum in the solid state of [Pd(Et,Pent timdt)$_2$] and the EQE of the corresponding device.

3.4 Dark currents and injection barriers

Efficiency and repetition rate at which we can detect a train of light pulses show a trend: as the energy gap decreases, they decrease too. This is mainly due to the increasing noise level, that limits voltage bias we can apply, thus limiting achievement of higher efficiencies; on the other hand, signal-noise ratio limits the repetition rate at which it's possible to detect a train of light pulses. Noise level increases because when energy gap narrows, injection barriers for charge carriers from the contact to the active material lower and dark currents growth.

The importance of the height of injection barriers, due to the alignment between Fermi level of metal contacts and HOMO and LUMO levels of the semiconductor [11], is underlined by experimental results. We realized three different devices based on the neutral dithiolene [Pt(Et,Pent timdt)$_2$] employing electrodes made of Pt, Au and Cr. Dark currents are minimized with Cr electrodes (Fig. 3, left); in fact, hybrid-DFT calculations of neutral dithiolenes HOMO and LUMO levels [7,8] show that injection barriers determined by the Fermi level of Cr are larger than those we have with Au and Pt.

We can increase injection barrier selectively for holes and for electrons by realizing a device with electrodes made of different metals with different Fermi levels; it's what we did in the P3HT based device, which exhibits lower dark current when reverse bias is applied (Fig. 3, right).

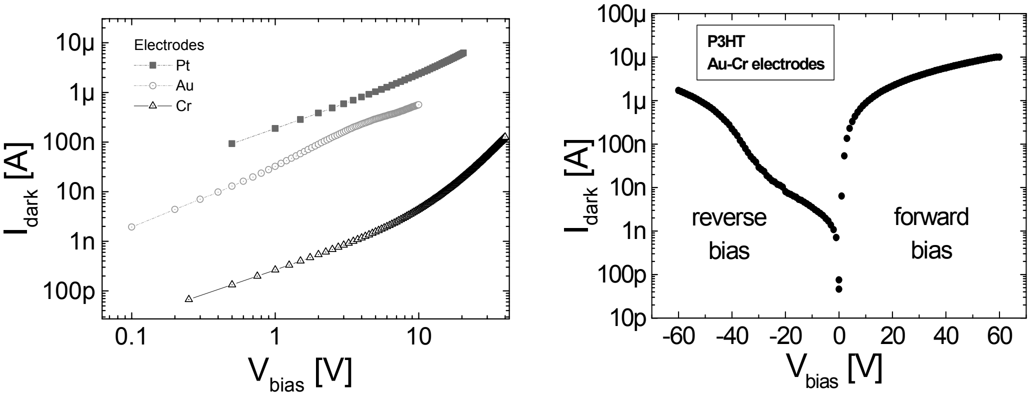

Fig. 3. On the left side, comparison of dark currents measured on three different devices based on the neutral dithiolene [Pt(Et,Pent timdt)2] with metal electrodes made of Pt, Au and Cr, spaced 12μm and with an effective width of 15mm. On the right side, dark current of the P3HT based device with one electrode made of Au and one of Cr.

4. CONCLUSIONS

We have demonstrated that organic materials can be employed to develop photodetectors sensitive to visible radiation and to the optical fiber windows. We fabricated prototype devices based on these materials and we illuminated them by trains of light pulses at different wavelengths and rates to test their performances. In Tab. 1 we resume experimental results.

We have demonstrated also the importance of a correct choice of the metal contacts in order to reduce noise level; this way is very promising in order to improve pulses detection rate. Efficiencies are actually limited, but blends of our sensitive materials with suitable moieties are under study in order to improve them.

Table 1. External quantum efficiencies and time response of photodetectors with spectral absorption matched to every examined spectral range, on planar structures. (a) L=6 μm, V_{bias}=–40V, Cr and Au contacts, λ=470nm. (b) [Pd(Et,Pent timdt)$_2$], L=12μm, V_{bias}=60V (108V for time response), Cr contacts, λ=840nm. (c) Diox3+, L=6μm, V_{bias}=12.5V, Cr contacts, λ=1280nm. (d) [Pt-Et,Et]$^-$ L=12μm, V_{bias}=40V, Cr contacts (time response was software averaged), λ=1450nm.

SPECTRAL RANGE	ACTIVE MATERIAL	EQE	TIME RESPONSE
Visible	P3HT (a)	0.5 %	4 Mbit/sec
First window	Neutral Dithiolenes (b)	$0.1*10^{-2}$%	200 Kbit/sec
Second window	Dioxolenes (c)	$0.4*10^{-2}$ %	10 Kbit/sec
Third window	Mono-reduced Dithiolenes (d)	$0.5*10^{-3}$ %	80 Kbit/sec

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