

Hybrid metal-organic photodetectors based on a new class of metal-dithiolenes

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Abstract

The paper will describe a new photodetector based on a metal-organic semiconductor material sensitive to the near IR region of the electromagnetic spectrum. The detector has a planar metal-semiconductor-metal structure with the active material deposited from liquid phase over a quartz substrate. Together with the fabrication process and the time response to light pulses, emphasis will be given to the intrinsic wavelength selectivity of the semiconductor material, of about 100nm around its peak sensitivity. The ease of deposition may enable to directly develop optical devices on passive optical component or on electronic substrates.

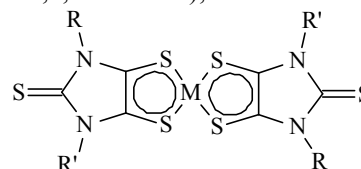
1. Introduction

The growth of interest toward organic electronic devices, motivated by their flexibility, luminescence in the visible range, large covered area and ease of fabrication, has led to the successful realization of light-emitting diodes [1-3], transistors [4,5] and phototransistors [6]. Concerning light-detecting devices, research and industrial interest has focused on photovoltaic cells [7,8], with very few attempts toward photodetectors for signal applications [9-11]. Their relatively slow time response has only recently been overcome by the presentation of a structurally sophisticated vertical multilayer photodetector, which, thanks to a thickness of a few tens of nanometers, has a response to single pulse within few nanoseconds [12].

In this paper we present a very simple planar photodetector device realized by mere casting of the active material. The performance of this device may help to rethink optical communication systems structure for certain applications.

2. Active material

The active material belongs to the new general class of neutral dithiolenes, $[M(R,R'timdt)_2]$ ($M = Ni, Pd, Pt$; $R,R'timdt$ = monoreduced form of 1,3-disubstituted imidazolidine-2,4,5-trithione),



whose synthesis has been reported elsewhere [13].

These dithiolenes exhibit an absorption band with large molar extinction coefficients around 1000 nm, good solubility in low polar solvents and excellent chemical and thermal stabilities. In addition, chemical tailoring of the spectral range of absorption is possible by changing the metal and the substituents R and R' at the nitrogen atoms. The effect of the change of the metal is shown in Fig. 1: a shift of 20 nm is obtained on passing from Ni and Pt to Pd.

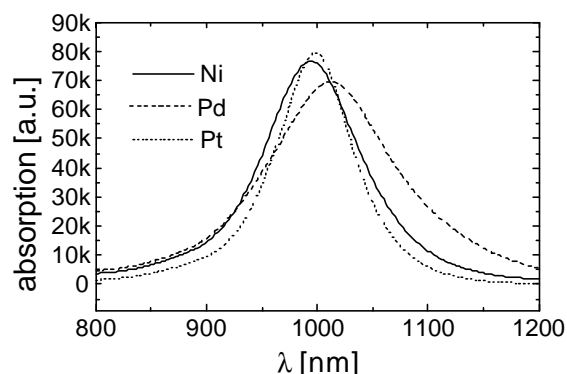


Figure 1. NIR absorption spectra of metal dithiolenes in chloroform solution for three different metal substituents (Ni, Pd, Pt). A shift of the absorption peak of about 20 nm is observed in the case of Pd complex.

3. Device structure and experimental setup

The device realized has a planar metal-semiconductor-metal structure. In contrast to vertical structures, surface structures have lower intrinsic capacitances, and therefore higher signal-to-noise ratio can be achieved. On the surface of a quartz substrate, Gold-Chromium interdigitated contacts, with Chromium acting as an adhesion layer, have been photolithographically defined. Interelectrode spacings of a few microns ($3\mu\text{m}$ or $6\mu\text{m}$) and electrode widths of 15mm have been realized. As the last step in device fabrication, the active material has been simply cast from a chloroform solution.

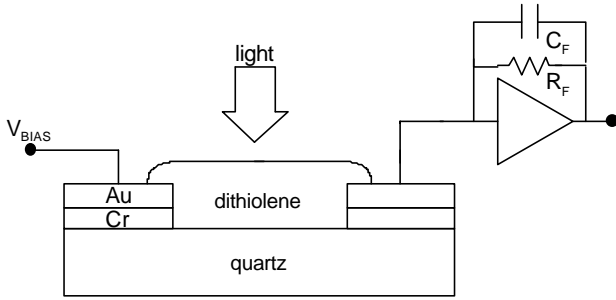


Figure 2. Schematic representation of the planar metal-dithiolene-metal photodetector prototype structure. The two contact electrodes are prepared with Chromium-Gold depositions on a quartz substrate. The active material is cast on top of the structure, light side. The device is connected to a transimpedance amplifier.

Measurements have been performed in air and at room temperature, by connecting the DUT to a low noise transimpedance amplifier. Commercially available LEDs have been used as pulsed light sources. Device structure and experimental set-up are schematically reported in Fig. 2.

4. Experimental results

The working principle of the photodetector is sketched in Fig. 3. In the active material excited states (excitons) are populated by the absorption of photons. Thanks to the external voltage bias, an electric field is present thus enabling excitons dissociation into electron and hole pairs which then drift to gold electrodes where they are collected.

Photogenerated carriers do not experience energy barriers at the metal-dithiolene contacts. On the other hand a barrier exists for carriers to be injected from the contacts into the active material, thus limiting the dark current of the device.

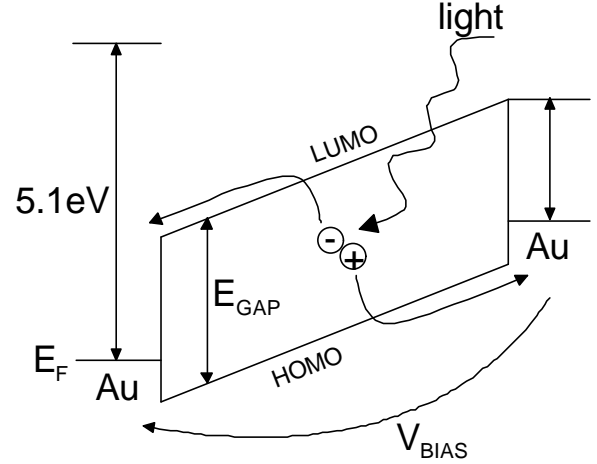


Figure 3. Principle of operation of the photodetector. Excitons created by the light pulse dissociate into electron and hole pairs which are collected by the gold electrodes. Relevant energy levels when an external voltage bias is applied are qualitatively shown.

Unfortunately, the choice of gold as metal limits the energetic barrier to a few tenths of electronvolts and non-negligible dark currents of several tens of nanoamperes are currently experienced for bias voltages in the range of some volts. In Fig. 4 a typical current voltage curve recorded in the dark is reported.

In Fig. 5 is shown a typical response of the photodetector biased and connected to the transimpedance amplifier. During the light pulse, indicated in shaded grey in figure, charge is photogenerated and collected on the feedback capacitance.

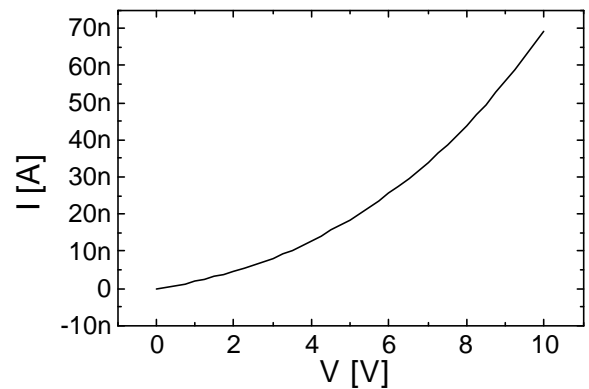


Figure 4. Dark current of a $[\text{Pd}(\text{Et}_2\text{timdt})_2]$ based photodetector, recorded with a HP4142B. Because of the poor energetic barrier between dithiolene and gold, a non negligible current flows.

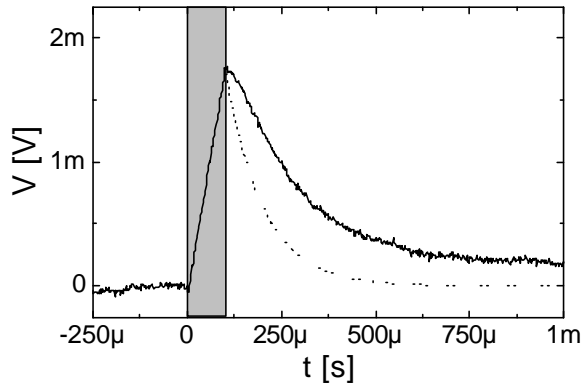


Figure 5. Response of a $[\text{Pd}(\text{Et}_2\text{timdt})_2]$ based photodetector biased at 4V to a $100\mu\text{s}$ light pulse at 880nm. $R_F=100\text{M}\Omega$ and $C_F=100\text{M}\Omega$. During the pulse, (grey shaded area), a constant photocurrent is integrated on C_F . The photogenerated charge is swept out after the light pulse, thus prolonging the output decay with respect to the mere discharge of C_F through R_F , which is reported as a dotted line.

An almost constant current is produced resulting in a linear increase of the output voltage.

When the light flash ends, the output voltage starts diminishing. The output voltage decay does not take place according to the mere discharge of the feedback capacitance through the feedback resistance (dotted line in Fig. 5), as it would occur if the photocurrent instantaneously dropped to zero. On the contrary, a current keeps flowing even after the pulse and the decay is considerably longer than the expected RC discharge. This is most probably due to the photogenerated charge accumulated in the device being swept out by the electric field.

The output voltage is an increasing function of the bias voltage applied to the photodetector. This occurs because the exciton dissociation is a field aided process, the higher the field the higher being the number of produced photocharges which can then be collected. In Fig. 6 a slightly superlinear behavior of the output voltage as a function of the average electric field applied to the photodetector is shown.

The dynamic behaviour of the detector for an impinging train of light pulses allows a bit rate of almost 10kbit/s. Figure 7 reports this possibility by showing the output signal from the transimpedance amplifier followed by a low-pass voltage amplifier when two light pulses (dotted line) with a time delay of $10\mu\text{s}$ are shone on the photodetector.

The limiting factors to a higher pulse rate are due, at present, to a low carriers mobility and to the presence of dark currents which, saturating the amplifier dynamics,

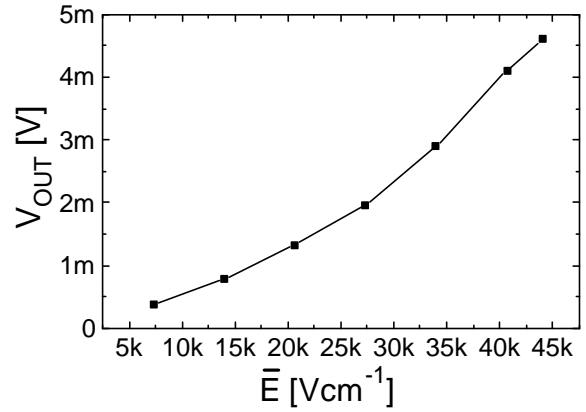


Figure 6. Output voltage as a function of the average electric field \bar{E} applied to a $[\text{Pd}(\text{Et}_2\text{timdt})_2]$ based photodetector, in case of a 1ms long light pulse at 880nm.

prevent to apply higher bias voltages and hence to reach higher dissociation efficiencies and shorter collection times.

An interesting feature of the device follows from Fig. 8. Data from photocurrent measurements (squares), performed at different incident wavelengths, are in good agreement with the absorption spectrum of the active material in chloroform solution (continuous line). Absorption of radiation from 400nm to 800nm is almost negligible with respect to the peak around 1000nm.

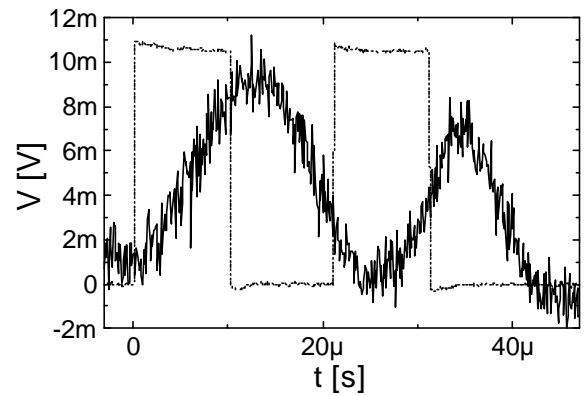


Figure 7. A $[\text{Pd}(\text{Et}_2\text{timdt})_2]$ photodetector is connected to a transimpedance amplifier followed by a low-pass voltage amplifier. The dotted line represents the two light pulses, $10\mu\text{s}$ long and $10\mu\text{s}$ delayed. The output signal has been averaged 4 times.

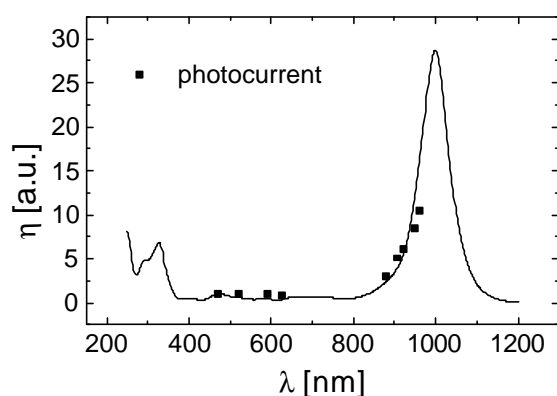


Figure 8. The continuous line is the absorption spectrum of $[\text{Pd}(\text{Et}_2\text{timdt})_2]$ in chloroform solution. Efficiency η from photocurrent measurements as a function of the incident wavelength is in good agreement.

The device is therefore acting as an intrinsically wavelength selective photodetector, particularly suited for near infrared applications.

5. Conclusions

Dithiolenes based photodetectors seem to be a very promising class of devices.

The active material has excellent chemical and thermal stability, a not so common feature in the emerging field of organic optoelectronics. It can be deposited from liquid phase on a wide range of substrates, thus enabling to directly develop devices on the cleaved surface of a fiber or onto the surface of optical splitters [14]. Such directly-on-optics-detectors could solve at its very roots the alignment problem.

The devices realized are intrinsically wavelength selective detectors with a time response of some tens of kbit/s. Improved performances could be attained by enhancing the rectifying characteristic of metal-semiconductor contacts.

At the moment, the changing of the metal and of the organic substituents R and R' at the nitrogen atoms has allowed to tune the position of the NIR absorption in a range of about 50nm. Efforts are currently devoted to the synthesis of new modified dithiolenes with the aim of shifting as much as possible the absorption peak further in the infrared region, so to better cover the spectrum of possible telecom applications.

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