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Large photoresponse from a small molecule: Application in photodetector and pseudo-transistor

Biswanath Mukherjee*

Department of Physics, Kalna College, Kalna, Burdwan 713409, India

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ABSTRACT

The observation of large photoresponsivity in a π-conjugated small organic molecule, *viz.*, N,N′-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C_8) and consequently, fabrication of organic photodetector with single layer of PTCDI-C_8 is reported. The same device, without any actual gate terminal, can also be used to obtain field-effect transistor (FET) characteristics by exploiting the photoresponse properties of the material. Photo-illumination on the active material which ensured an induced channel by the photo generated charge carriers, resembled as the pseudo gate electrode. The simple lateral structure with gold (Au) as source and drain electrodes and vacuum deposited thin film of PTCDI-C_8 as the active layer produced high-performance photodetector and transistor behavior, showing pseudo-output and transfer curves with an on/off ratio of 4×10^2. The two terminal organic devices exhibited photoresponsivity value *ca.* 50 mA/W, external quantum efficiency ~40%, reproducible and reversible photo-switching behavior with photo to dark current ratio *ca.* 200 and a switching time <10 ms. Modulation and tuning of the device's performance were done by controlling the number of photo generated carriers. The multifunctional ability, such as, photosensing, photoswitching, and signal amplification realized in a single unit opens up immense possibilities for integrated device applications in large-scale and low-cost plastic optoelectronic devices.

1. Introduction

In recent years, there have been significant developments in the performances of organic semiconductor based devices, bringing them even closer to compete to their inorganic counterparts and/or replace them. The advantages offered by the organic devices are many folds, which includes low fabrication cost, smaller size, simple fabrication method, large area coverage, 3-D stacking, low processing temperature, inherent tunability by tailoring of chemical structure and mechanical flexibility compatible with plastic substrates [1,2]. As a result, molecular electronics are now gaining renewed research attention and immense interest has been paid for the fabrication of high-performance organic devices. Moreover, as a solution to the scaling limit issue along with a number of other added advantages, it is now being considered as a suitable replacement of the traditional silicon microelectronics technology.

Organic field-effect transistors (OFETs), which form the basic building block for many electronic devices and circuits, such as identification tags, smart cards, electronic paper [3–5], have witnessed dramatic improvement in the performance limit in the last two decade. Apart from the high mobility OFET (mobility exceeding 5 $cm^2 V^{-1} s^{-1}$) [6,7], high-efficiency organic solar cells [8], organic memory devices [9], organic light emitting diodes [10,11], sensors [12,13] have been successfully demonstrated to exhibit excellent performance. Additionally, the high photoresponse of some organic semiconductors enables the fabrication of two-terminal organic photodiode/photodetector (OPD) [14–17] and three-terminal organic phototransistors (OPTs) [18–21]. OPT is a kind of multifunctional optoelectronic device, where additional photo-carriers could be generated by exposing the active medium with external illumination, resulting in efficient charge transport through the device and leading to highly photo-responsive switching device [18–20]. In OPD also, photo-illumination can be exploited as the pseudo-gate electrode to make the device functioning both as photosensor and transistors [17]. OPDs, in the context of information-conversion applications, are advantageous due to their ability for large surface area light detection, wide selection of materials allowing color tuning, and cheap fabrication methods [22]. The organic photodiodes with high photosensitivity are normally either multilayer-heterojunction type [23] or bulk-heterojunction type [24]. In the present study, we have fabricated two-terminal, lateral, single layer organic photodetector and

* Tel.: +91 03454 255032; fax: +91 03454 255169.
E-mail address: biswanath.mukh@gmail.com

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demonstrated how the same device structure could function both as photodetector and pseudo-transistors. By fabricating planar structure, we also have avoided the deposition of top electrode by thermal evaporation which may penetrate through the film leading to electrical shortening of the device.

It is quite obvious that for maximum quantum yields and high photocurrent densities, the rigid, planar structure of the molecule and coplanar device structure is a pre-requisite condition. This will result in effective absorption of incident light and the photoexcitation for the photodetector device [25]. Since the photoresponsivity of the device depends on the photogeneration efficiency, exciton dissociation, carrier diffusion and charge extraction mobility of the active organic material, the carrier mobility of the material should have high value as well as the optical absorptions of the material should cover a broad spectral region. Also, because of shorter exciton diffusion length in organic semiconductor, it is desirable to have strong optical absorption such that the ratio of the exciton diffusion length to the optical absorption depth can approach unity [26]. The material (PTCDI-C_8) chosen for the present work fulfills both the conditions. Additionally, the material could be deposited by thermal vacuum-deposition method, where, the thickness control of the active thin film can efficiently be done with ease and hence high current gain can be obtained in the device. We have shown in this manuscript that the two terminal planar devices can also be used to obtain the (pseudo) characteristics of the transistor device with intensity of the incident illumination as the pseudo gate terminal. Without a gate electrode, the two-terminal device showed pseudo-output/transfer characteristics with photoinduced *n*-channel having an on/off current ratio of *ca.* 4×10^2. The device, upon pulsed illumination of incident radiation, exhibited excellent photoswitching characteristics with maximum photo to dark current ratio as high as 200 and photoswitching speed of <10 ms. The intensity of the incident illumination was shown to have considerable impact on the on/off current ratio so as to modulate the device performances by an appreciable amount.

2. Experimental

The active organic semiconductor, used for this study, that is, N,N′-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C_8) was purchased from Aldrich Chemicals and was used as received. The two terminal pseudo transistors were fabricated on cleaned SiO_2/Si substrates. For comparison, we also have fabricated three terminal OFETs on the same substrate in bottom-gate, top-contact source–drain electrode configuration. n^+-Si (1 0 0) wafers with thermally oxidized SiO_2 layers (300 nm) was used as the gate electrode and gate dielectric respectively. On top of the dielectric, organic semiconductor (PTCDI-C_8) was vacuum deposited (50 nm) at a rate of 0.3 Å/s and at a base pressure of 5×10^{-6} Torr. Finally, gold (Au) was thermally evaporated through a shadow mask on top of the PTCDI-C_8 film to make top contact source–drain electrodes (40 nm) under a high vacuum (5×10^{-6} Torr) at a rate of 0.3 Å/s. The channel length (L) and channel width (W) of all the devices were measured to be 30 μm and 1000 μm, respectively. An HP4145B semiconductor parameter analyzer controlled by locally written LabView codes through a GPIB interface was used for the electrical characterization of the devices under ambient conditions. For the characterization of the devices under white illumination, a common incandescent lamp (white LED) was employed as a light source. The external quantum efficiency (EQE) of the devices was measured using the incident light from a xenon lamp passed through a monochromator. UV–Vis absorption spectra of the organic thin film on quartz substrate was measured with a Shimadzu UV-3101PC spectrophotometer.

3. Results and discussions

A schematic of the two terminal, lateral photodetector device is presented in Fig. 1a, and the chemical structure of PTCDI-C_8 is depicted in Fig. 1b. The device structure shows that the light is illuminated directly on the active material from the top to ensure maximum exposure of the incident radiation. Here, the lateral electrodes (Au) deposited on the film can act as source–drain contacts while the externally illuminated visible light played the role of pseudo third (gate) electrode. The two-terminal organic pseudo transistors were realized using "the photoinduced *n*-channel" effect, rather than voltage induced charge accumulation. The non-contact mode of third electrode not only reduces the cost of yet another metal deposition and fabrication time, but protects also the active organic layer from excess heat and nullifying the interfacial effects between gate and the semiconductor.

Fig. 2 shows the current–voltage (I–V) characteristics of the photodetector device in dark and under light illumination. The intensity of the light was fixed at 15 mW/cm^2 during continuous exposure to the active film. Fig. 2a shows that the current under illumination was much greater than that in dark. It can also be seen from the log–log plot of I–V curve (Fig. 2b) that the photo current of the device is more than two orders of magnitude higher than the dark current. The linear nature of the curves also indicated that an ohmic contact might be established at the junction between the electrodes and the semiconductor. It is very much essential for any optical device to have large photo/dark current ratio in order to avoid any misreading/error between different states in digital circuits. For the present device the ratio is moderate, and can further be improved by decreasing the channel length (gap) between the electrodes. An important attribute of photodetector device is photoresponsivity (P), which can be defined by the following equation:

$$P = \frac{I_{\mathrm{Ph}} - I_D}{P_{\mathrm{in}} \times S}$$

where I_{Ph} and I_D are the device current with and without illumination, P_{in} is the incident optical power and S is the effective device

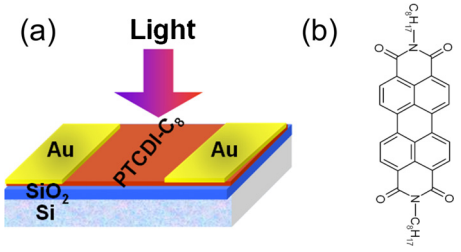

Fig. 1. (a) Schematic representation of two terminal photo-gated organic transistors. (b) Chemical structure of N,N′-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C_8).

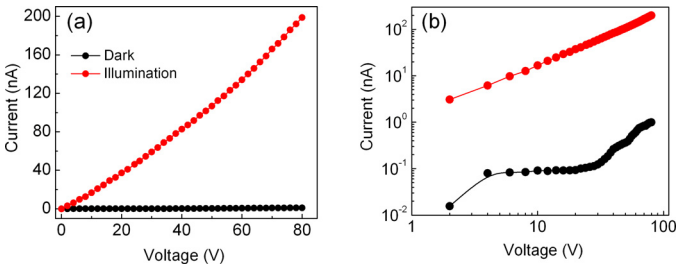

Fig. 2. Current–voltage characteristics of the photodetector in dark and under illumination (15 mW/cm^2) in (a) linear and (b) double log scale.