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Optoelectronic conversion by polarization current, triggered by space charges at organic-based interfaces

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We report that a highly efficient optoelectronic conversion can be achieved by photogenerated space charges, which usually damp photocurrent. Theoretical analysis of metal-organic insulator-organic semiconductor-metal photocells indicates the generation of a large transient current that is triggered by photogenerated space charges and governed by the dielectric properties of the insulator layer. We experimentally demonstrated this mechanism with model photocells, revealing that the quantum efficiency can be dramatically increased by increasing the dielectric constant of the insulator. © *2010 American Institute of Physics*. [doi:10.1063/1.3454915]

While conventional optoelectronic conversion (OEC) is usually based on photoelectric emission, photoconductive, photovoltaic and pyroelectric effect in inorganic materials, organic optoelectronics devices (ODs) have received recent attention due to, among other things, their low cost, light weight, and ease of fabrication. However, attempts to substitute the inorganic materials in ODs with organic materials always encounter the most significant problem with organic materials, namely, their poor mobility. Due to this and an imbalance between hole and electron mobilities, space charges are always produced in organic ODs such as organic solar cells[1,2] and photodetectors (PDs),[3–5] thus limiting the photocurrent in these devices.[6] However, it is also notable that the photogenerated space charges can boost the OEC through generation of a highly efficient transient photocurrent (TPC), as we have demonstrated previously.[7]

In the present work, we developed a light detection principle for OEC based on a metal/organic insulator/organic semiconductor/metal (MISM) structure. The organic double layers between the metals induce an imbalance of carrier transports, which facilitates the generation of space charges. The dielectric polarization in the insulator, triggered by the space charges, magnifies the TPC in the semiconductor layer. The OEC increases with increases in the dielectric constant of the insulator layer. The obtained performance is highly applicable to pulse light detection in many systems such as optical communication devices and image sensors.

Figure 1(a) shows the present OD, which consists of a charge separation layer (CSL), a blocking layer (BL), and two noninjecting electrodes. The CSL is composed of organic semiconductor(s), which exhibit an effective charge separation upon illumination, while the BL is made of a transparent insulator and can suppress the dark current. The CSL thickness d_s is far less than that of BL, d_i, and is also smaller than the drift length of the carriers. It is expected that, after charge separation in the CSL, either the hole or electron can be collected by the electrode, while the other is accumulated at the BL/CSL interface. This separation of electrons and holes leads to a polarization current in the BL and a discontinuity of the electric field at the BL/CSL interface, as schematically illustrated in Fig. 1(a).

We have theoretically analyzed this dynamic process of the space charges, using a double-layer model. The details

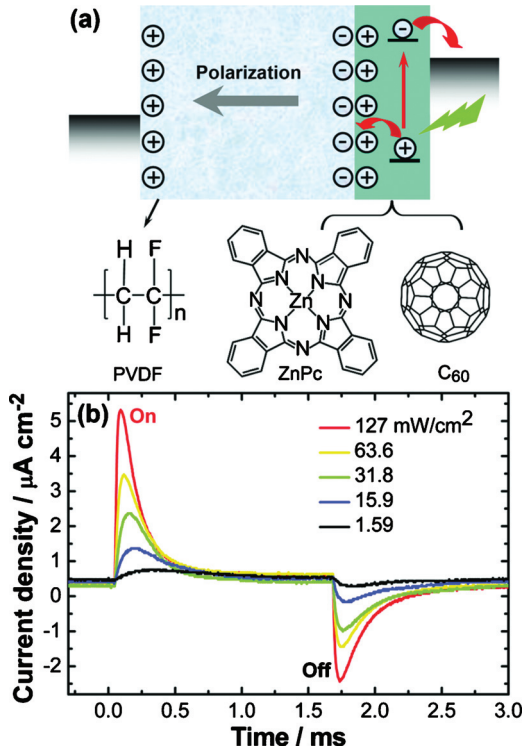

FIG. 1. (Color) (a) A schematic display of a double-layer model for an anode/BL/CSL/cathode photosensor, in which photogenerated electrons in the CSL are collected by the cathode and the accumulated holes at the BL/CSL interface, triggering a polarization current in the BL. The inset shows the chemical structures of PVDF and ZnPc:C_{60} donor-acceptor (1:1) systems. (b) The photoresponse of an ITO/PVDF (1 μm)/ZnPc:C_{60} (30 nm)/Al photocell under illumination from a modulated 532 nm laser (300 Hz) with different intensities. The sample was illuminated from the ITO side under a bias voltage of 0 V.

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are described in Ref. 8. After considering the total current equation,[9] the external photocurrent is found to be expressed as

$$i(t) = \frac{S\xi}{(\tau - RC)}(e^{-(t/\tau)} - e^{-(t/RC)}),$$

$$\text{with} \quad \xi = \varepsilon_0 \varepsilon_i^{\,2} d_s V / d_i(d_i\varepsilon_s + d_s\varepsilon_i)$$

$$\text{and} \quad \tau = \varepsilon_0(d_i\varepsilon_s + d_s\varepsilon_i)/d_i\sigma_s^{\,*}, \tag{1}$$

where S is the effective area of the photocell, R is the voltage drop across load resistor, C is the capacitance of the photocell, ε_0 is the vacuum dielectric constant, ε_i and ε_s are the relative dielectric constants in the BL and CSL, respectively, and $\sigma_s^{\,*}$ is the photoconductivity in the CSL. The parameter V is the bias voltage, written as $V = E_i d_i + E_s d_s$. Therefore, the largest current density $J_{tr}^{\,0}$ can be achieved, which is expressed as

$$J_{tr}^{\,0} = \frac{\xi}{(\tau - RC)}\left(\frac{RC}{\tau}\right)^{RC/(\tau - RC)}\left(1 - \frac{RC}{\tau}\right). \tag{2}$$

It is notable that $J_{tr}^{\,0} \propto \varepsilon_i^{\,2}$, if $d_i\varepsilon_s \gg d_s\varepsilon_i$ in Eq. (2). As such, we can magnify the TPC by increasing the dielectric constant in the BL. This change provides us with a way of magnifying the OEC in organic photosensors.

To check the above mechanism, an equivalent MISM junction cell was fabricated with indium tin oxide (ITO) and aluminum (Al) electrodes. A well-known polymer, polyvinylidene fluoride (PVDF) (8 wt % in dimethylformamide), was adopted for the BL and was spin-coated onto a hot ITO glass slide (100 °C). The thickness was estimated to be ~1 μm by cross-sectional SEM images. On the top of the BL, a 30 nm CSL with a high charge-separation efficiency was prepared with zinc phthalocyanine (ZnPc) and fullerene (C_{60}) (molar ratio: 1:1, see Fig. 1(a) for their molecular structures) by codeposition under a vacuum of ~4×10^{-4} Pa with a rate of 1 Å/s. The Al cathode (60 nm) was then thermally evaporated onto the blend film with an effective area of 0.02 cm^2. All the materials are commercially available. The photocurrent measurements were carried out under an illumination from a green laser (532 nm) controlled by a multifunction synthesizer.

The photoresponses across a load resistor of 10^5 Ω were recorded on an oscilloscope. The results are shown in Fig. 1(b) with various light intensities. Upon laser illumination, a large TPC is produced, and a negative TPC appears just after the illumination. Both the positive and negative TPC increase with increases in the light intensity. Continuous current oscillation induced by a frequency modulation is stably observed without degeneration [see Fig. S1(a)]. A good agreement of peak positions in the absorption and photocurrent-action spectra[8,10] [see Fig. S1(b)] suggests that CSL is the sensitive component.

The blue triangles in Fig. 2(a) show the time dependence of the current density of the positive TPC obtained under an illumination of 31.8 mW/cm^2. The solid red curve in this figure shows the theoretical results from Eq. (1) with an RC time constant of 4.2×10^{-5} s, which was experimentally determined for the present circuit by an LCR meter at 100 Hz. The theoretical results explain the experimental data very well, and τ is estimated to be ~2.5×10^{-4} s during which $1-(1/e)$ of the photogenerated carriers will be collected by

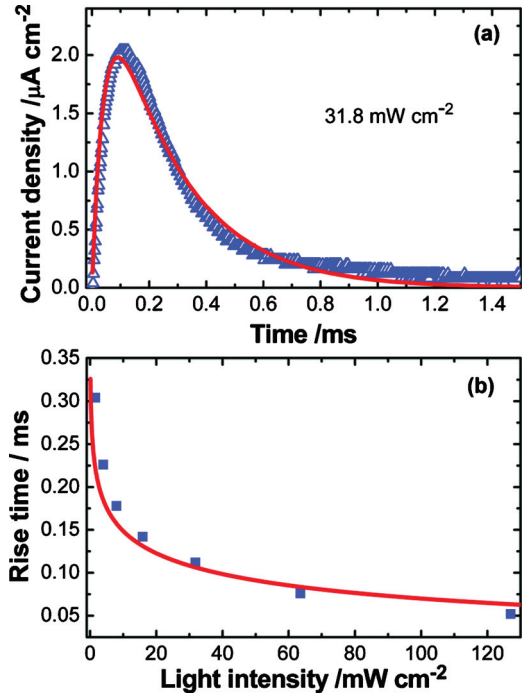

FIG. 2. (Color) Simulations for the positive TPC based on (a) Eq. (1) and (b) Eq. (S5) with an RC time constant of 4.2×10^{-5} s at 100 Hz. The red lines are theoretical data and the blue points are experimental data from Fig. 1(b).

electrodes. The blue squares in Fig. 2(b) depict the dependence of the rise time τ_R on the light intensity. This behavior is also reproduced by Eq. (S5) (solid curve) with $\tau \approx 4.7 \times 10^{-4}$ s under an illumination of 31.8 mW/cm^2, using the same RC time constant. This value is in approximately agreement with that obtained by Eq. (1).

To examine the relation between the dielectric constant ε_i of the BL and the quantum efficiency of TPC, we prepared photocells with three different BLs, namely, with vacuum gap ($\varepsilon = 1$), polystyrene ($\varepsilon \approx 2.6$),[11] and PVDF ($\varepsilon \approx 7-13$).[12] The fabrication method for the polystyrene BL was the same as that for PVDF. The thicknesses of CSLs are approximately 20 nm. Considering that both the dielectric constants of ZnPc and C_{60} are around 4.0 which is comparable to that of BL and the d_s is much smaller than d_i, the condition $d_i\varepsilon_s \gg d_s\varepsilon_i$ for $J_{tr}^{\,0} \propto \varepsilon_i^{\,2}$ can be easily satisfied. Figure 3 shows the short-circuit photoresponses of the three cells against a strong illumination (160 mW/cm^2). The values of TPC dramatically increase with ε, as is predicted from Eq. (2). As such, we can control OEC by changing the ε value of BL. The positive $J_{tr}^{\,0}$ of the PVDF photocell is ~8×10^2 times larger than that of the vacuum-gap photocell, though a rough estimation based on Eq. (2) suggests a difference of two orders of magnitude. The internal quantum efficiency of TPC in this PVDF cell under a weak illumination (0.2 μW/cm^2; 560 nm) from a halogen lamp is calculated to be approximately 34% [root mean square, (rms)]. The photoresponsivity at 560 nm (0.2 μW/cm^2) reaches 10 mA/W (rms) even without applying a bias voltage, which is comparable to those of conventional organic PDs operated by a bias voltage.[10,13,14]

To evaluate the lifetime of TPC, an impulse response was examined with a nanosecond laser beam (600 nm) from an optical parametric oscillator pumped by a neodymium-doped yttrium aluminum garnet laser (pulse width: ~6 ns;

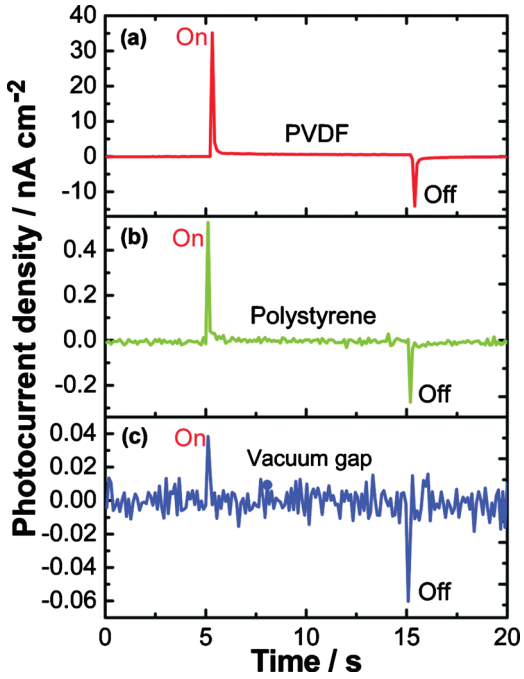

FIG. 3. (Color) The dielectric constant dependence of the TPC under an illumination (532 nm) of 160 mW/cm^2. (a)–(c) show the short-circuit TPC in the MISM photosensor with PVDF, polystyrene, and vacuum gap as BLs, respectively. The thickness of the BLs and CSLs are ~1 μm and 20 nm, respectively.

power: ~1.08 μJ/pulse). A digital oscilloscope with a bandwidth of 1 GHz and a dc 300 MHz amplifier were used to collect the voltage response with an input resistance of 50 Ω. Figure 4 shows the impulse response of the photocell with a 1 μm PVDF BL, which consists of rise, decay, and recover processes. This behavior is similar to that of the pyroelectric detectors with slower rise, decay and recover times,[15,16] though their mechanisms are quite different. The rise and decay time of the present photocell were found to be ~15 and 100 ns, respectively. Both the rise and decay times show an RC constant dependence; they increase with increases in the RC constant (not shown), which can also be roughly checked from Fig. 1(b) with a resistance of 10^5 Ω and Fig. 4. However, the recover time exhibits a long time scale of ~2.5 μs (see the inset of Fig. 4) and is independent of the RC constant. A faster response can be achieved by decreasing the ε of BL. For example, substitution of the

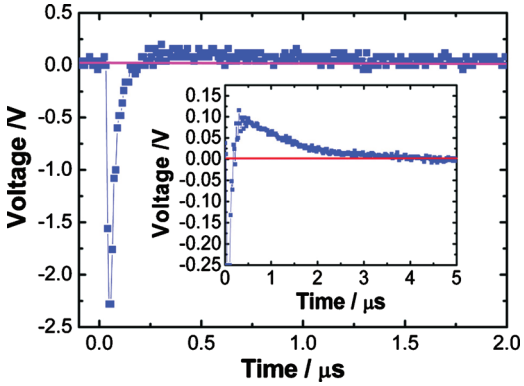

FIG. 4. (Color) Impulse response of the ITO/PVDF (1 μm)/ZnPc:C_{60} (20 nm)/Al photosensor under a zero bias voltage. The RC constant in this circuit was estimated to be ~5 ns. A nanosecond laser (10 Hz; 600 nm; ~1.08 μJ/pulse) with a pulse width of ~6 nm was utilized. The inset is a magnified version of the recovery process.

PVDF layer with polystyrene brings about a much faster rise (~5 ns) and decay (~8 ns) times at 0 V, but the recover time is still ~1 μs. This slow recovery time could be ascribed to an energy barrier between the donor-acceptor and/or semiconductor-metal interfaces. Considering that the polarization current is proportional to the variation rate of E_i triggered by the photogenerated space charges, a faster generation of space charges by a sharper light pulse can bring about a larger TPC, even when only a small number of space charges are generated. Therefore, the device speed is mainly determined by the rise and decay time, even though the system does not completely recover.

In summary, we have proposed and confirmed an OEC with an organic-based MISM structure immune from pinhole effects which usually exist in ultrathin metal/semiconductor/metal devices. This is a mechanism to detect pulsed light, in which the space charges of the organic materials are regarded as a merit, and may also be employed to explain some similar phenomena, i.e., the so-called anomalous photocurrent in some materials.[17–19] Model photocells with the MISM structure exhibited a large TPC even without a bias voltage, and the time trajectory was well-explained by the theoretical model. The transient OEC was dramatically increased by increasing the dielectric constant of the BL. These results suggest a light detection principle for various fields, including communications, remote control and image sensors.

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