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The role of local potential minima on charge transport in thin organic semiconductor layers

Egon Pavlica, Raveendra Babu Penumala, Gvido Bratina*

Laboratory of Organic Matter Physics, University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia

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ABSTRACT

We have performed a systematic study of dependence of time-resolved photocurrent on the point of charge excitation within the organic semiconductor channel formed by two coplanar metal electrodes. The results confirm that spatial variation of electric field between the electrodes crucially determines transport of photogenerated charge carriers through the organic layer. Time-of-flight measurements of photocurrent demonstrate that the transit time of photogenerated charge carrier packets drifting between the two electrodes decreases with increasing travelling distance. Such counterintuitive result cannot be reconciled with the spatial distribution of electric field between coplanar electrodes, alone. It is also in contrast to expected role of space-charge screening of external electric field. Supported by Monte Carlo simulations of hopping transport in disordered organic semiconductor layer, we submit that the space-charge screens the external electric field and captures slower charge carriers from the photogenerated charge carrier packet. The remaining faster carriers, exhibit velocity distribution with significantly higher mean value and shorter transit time.

1. Introduction

Photoconductivity of organic semiconductors (OSs) is characterized by relatively high photon-to-charge conversion efficiency and low charge carrier mobility [1]. As a result, the photogenerated charge carriers accumulate within the OS layer as a space-charge, which effectively screens externally applied electric field. Consequently, effective charge carrier velocity and therefore their current through the layer, is reduced. Theoretical description of this phenomenon is known as the space-charge-limited current (SCLC) model [1,2]. At the core of the SCLC model is the concept of the distribution of localized states, which trap the carriers during charge transport. Based on the SCLC model, several experimental methods were developed in order to investigate space-charge effects on the charge transport [3]. Most of them focus on bulk materials, where space-charge screens externally applied electric field between a pair of parallel electrodes. Typically, in such configuration space-charge accumulates near the injecting electrode due to the low charge-injection barrier. For a recent review of studies of space-charge effects in OS thin layers embedded between two coplanar electrodes see for example Ref. [3]. Charge transport in thin OS layers is hindered by charge carriers, which accumulate near the low-barrier electrode [4,5]. Consequently, mobility of the injected charge carriers through the OS layer is reduced and their effect on local electric field is only minor [6].

In contrast, photogenerated charge, which is not injection-limited, represents a significant transient perturbation of the local electric field [1]. Ligthart et al. recently demonstrated that space-charge is the reason for relatively long relaxation time of organic photodiodes [7]. Pivrikas et al. studied photocurrent generation in conjugated polymers as a function of light intensity [8,9]. Their findings confirm that photogenerated carriers alter electric field in the polymer layer. Danielson et al. used the photoconductivity measurements in thin OS layers to probe the charge transport and recombination in bulk-heterojunction layers, used as a part of organic solar cells [10].

In this work we used photoconductivity measurement to study space-charge effects on charge carrier transport in thin OS layers. We used time-of-flight (TOF) photoconductivity method due to its extreme sensitivity to charge transport perturbations, as previously demonstrated on reduced graphene oxide layers [11]. TOF measurements yield information on charge carrier transport in semiconducting as well as in insulating materials [12]. They are selective for different charge polarity, changes in density of states [13], and

* Corresponding author.
E-mail address: gvido.bratina@ung.si (G. Bratina).

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can be used to directly determine charge carrier velocity in OS layers [14]. TOF measurements are immune to the processes in the microscopic environment of a OS/metal interface. At the core of the technique is the electron-hole pair photoexcitation in an OS layer embedded between two coplanar electrodes, followed by the charge separation due to the externally applied electric field. The resulting drift current through the organic layer is monitored as a function of time. The velocity of photogenerated carriers is estimated from their drifted distance and the duration of induced current transient. Also other transport parameters can be estimated from the time dependence of the photocurrent, including charge carrier mobility, space-charge effects and photon-to-charge conversion efficiency [1,9–14].

TOF experiments can be performed on samples, in which the OS layer under investigation is sandwiched between two electrodes, of which one is transparent [12]. Such sample structure is not suitable for characterization of OS layers with thickness smaller than 1 μm [15]. This is because photon absorption exponentially decreases with depth of OS layer [16], and because of substantial leaking currents arising from large capacitance coupling between the electrodes [15].

An alternative to the sandwich-type samples are the samples, in which organic layer is placed between the two coplanar electrodes, similarly to the organic field-effect transistor (OFET) structures [17–21]. In contrast to sandwich-type samples, the electric field between coplanar electrodes is seldom spatially uniform [5,22]. Therefore, the interpretation of TOF photocurrent transients measured in these samples in terms of sandwich-type TOF measurements could lead to an underestimation of charge carrier mobility and misunderstanding of the charge transport mechanisms [22]. In our previous work [22], we introduced a model based on a displacement current [23], to calculate the photocurrent time dependence of a coplanar-type TOF measurement.

The displacement-current theory of the coplanar-type TOF measurement describes the time dependent photocurrent (I(t)) as a phenomena, which stems from the time variation of the charge induced on the electrodes [22,24]. Charge is induced on the electrodes by the displacement field of the photogenerated hole-electron pairs. The amount of induced charge per unit of photogenerated charge is introduced as the "weighting" potential (U_W), which depends on the position of the photogenerated charge and depends solely on spatial arrangement of the electrodes. As the photogenerated carriers drift in the electric field between electrodes, U_W and the amount of induced charge vary. As a result, photocurrent exhibits a time transient, determined by the time derivative of the product of the photogenerated charges and corresponding U_W. I(t) therefore depends on charge carrier velocity, which is determined by the spatial distribution of the electric field and a constant factor defined by the position of the selected charge carrier relative to the position of the electrodes.

We have performed coplanar-type TOF measurements in a thin layer of a semiconducting polymer of poly(3-hexylthiophene-2,5-diyl) (P3HT). We choose P3HT because it is a thoroughly investigated π-conjugated polymer [25], which exhibits field-effect mobility as high as 0.05 cm^2/Vs in highly purified OFETs [26], and power conversion efficiency up to 6.4% in organic solar cells [27]. Due to disordered structure of P3HT layers deposited from a solution, charge carrier transport must be described with a hopping-transport model.

We developed kinetic Monte Carlo simulation based on the Gaussian disorder model and hopping charge transport [22]. The simulations are used to interpret TOF measurements in a P3HT layer between coplanar electrodes. Next, we present a systematic study of the role of illumination position on the time dependence of TOF photocurrent in P3HT layer between coplanar electrodes. For that purpose, we have measured I(t) by varying the illumination position from biased electrode to the opposite electrode for both positive and negative bias voltages. Finally, we compare MC simulations with experimental data and discuss the effect of space-charge on the I(t) dependence.

2. Experimental

20 nm-thick P3HT layers were prepared by spin-coating a 4 mg/ml chloroform solution at 3000 rpm for 1 min on glass substrates. Two 100 nm-thick Al coplanar electrodes were deposited by vacuum evaporation through a shadow mask. The interelectrode separation (L) was 125 μm. We will use the OTFT nomenclature and refer to the interelectrode region as "the channel". Samples were thermally annealed at 150 °C for 5 min before characterization. TOF measurements of I(t) were performed using 4 GHz probe tips and 2.5 GHz oscilloscope as schematically presented in Fig. 1a. A constant bias voltage V_b was applied to the left electrode, from now on referred-to as the "biased" electrode. The opposite electrode labeled "sensing" electrode, was connected to a resistor (R) of 100 kΩ. I(t) of the photoexcited carriers was measured as a voltage drop over R. The selected value of R was a minimum, which allowed detection of the photocurrent, while maintaining the electric field between the electrodes unchanged. The charge carriers were excited by a pulsed laser with pulse duration of 3 ns, and a repetition rate of 3 Hz. Full-width at half-maximum intensity of the laser line was 20 μm, as measured with a commercial camera sensor (Fig. 1b). We selected photon energy of 2.34 eV, which corresponds to the maximum light absorption in P3HT. The incoming laser beam was focused perpendicularly onto the polymer layer surface with a cylindrical convex lens (Fig. 1a). The lens focused laser light into a narrow line, which was aligned along the electrode edge at a varying distance (x_i) from the biased electrode. The width of the illuminated area was approximately five times smaller than L. Two distinct laser pulse light intensities were used to illuminate the polymer. The number of photons per pulse was estimated by comparing the maximum of the measured I(t), and I(t) obtained by the Monte Carlo simulations (see below). The corresponding numbers of photons per pulse were $7.2 \cdot 10^7$ for low intensity and $1.6 \cdot 10^8$ for high intensity.

3. Results and discussion

Photogenerated charge carriers moving in a P3HT layer embedded between two coplanar electrodes (Fig. 1a), which are at different potentials due to the applied bias voltage V_b, induce variation of charge and current on the electrodes [23,24,28]. Time evolution of charge and current, therefore reflects dynamics of the charge carriers drifting in the inter-electrode electric field. The potential difference of the two electrodes, determines the direction of velocity of the holes and the electrons. This allows us to discriminate the contributions of the holes and electrons to I(t). For positive V_b, electrons drift to the biased electrode and for small values of x_i contribute only a fraction of current in to the I(t) curve, while holes drift away from the biased electrode, and contribute to I(t) during their travel through the channel. For negative values of V_b holes drift to the biased electrode and electrons drift to the sensing electrode. As we have shown previously by numerically solving Poisson equation for biased coplanar-electrode structures [22], the corresponding electric field (E(x)) inside the channel decreases rapidly with the distance from the electrode ($\approx (x/L)^{-\frac{1}{2}}$ within 10 μm). Further into the channel the decrease with the distance is considerably slower. The carriers that are generated near the biased electrode initially exhibit high acceleration due to high E(x). This is manifested in the I(t) line shape as an initial surge. As