Organic Electronics 34 (2016) 218–222

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Space charge limitation on the response time of organic photodiodes

Aart Ligthart [a], Gerwin H. Gelinck [a, b], Stefan C.J. Meskers [a, *]

[a] Molecular Materials and Nanosystems and Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[b] Holst Center, 5656 AE Eindhoven, The Netherlands

ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form
16 April 2016
Accepted 19 April 2016
Available online 29 April 2016

Keywords:
Organic photodiodes
Space charge limited current
Organic photovoltaics
Photo-impedance spectroscopy
Response time

ABSTRACT

The dynamic response of an organic bulk heterojunction photodiode to small changes in applied bias or light intensity is investigated as function of the intensity of a constant background illumination by means of photoimpedance and transient photocurrent measurements. For bias voltages close to the open circuit voltage we find that the response timescale with the square root of the light intensity. The results can be quantitatively explained in terms of a space charge limitation on the photocurrent as predicted by Goodman and Rose (*J. Appl. Phys.* **42**, 2823 (1971)). The relaxation time of the diode at open circuit corresponds to the lifetime of the slowest charge carrier in the diode. This relaxation time is determined by the dielectric constant and the smallest of the two carrier mobilities in the bulk heterojunction. This illustrates the importance of balanced carrier mobilities for obtaining diodes with fast response time at low bias for e.g. imaging arrays.

1. Introduction

Organic photodiodes with a bulk heterojunction between electron donor and acceptor material as active layer, can be used in imaging applications [1–8]. In some applications the diodes are operated without applying external bias. These include charge coupled device (CCD) array detectors, where the absence of applied bias helps to suppress the dark signal [9]. Furthermore organic photodiodes can be applied in self-powered artificial retinas [10,11]. These artificial retinas are used as prosthesis, to restore vision in patients [12–15]. The photodiode needs to generate a voltage that can trigger depolarization of the membrane of a nerve cell in the retina and give rise to a nerve pulse travelling towards the visual cortex. Obviously, in such an *in vivo* application, the photodiode cannot be powered by an external source. These applications raise the fundamental question as to which material properties determine the response time of the photodiode to changes in light intensity at low bias voltages.

The organic semiconductors used in the diodes are characterized by low carrier mobilities ($\mu \ll 1\ cm^2\ V^{-1}\ s^{-1}$) and low dielectric constants ($\varepsilon_r \approx 3$–4). The low mobility implies that photogenerated carriers can easily pile up in the diode, while the low dielectric constant means that electrostatic interactions between the charged carriers are hardly screened. Accumulation of photogenerated carriers [16] results in the built-up of space charge that can limit the response of the photodiode. Already in 1970, Goodman and Rose demonstrated space charge limited photocurrents in diodes featuring low mobility semiconductors [17]. For organic photovoltaic diodes space charge limited, steady-state photocurrent was demonstrated experimentally by Mihailetchi et al. [18] DiNuzzo et al. [19] showed that photoconductivity and photocapacitance under alternating electrical bias are space charge limited when organic photovoltaic diodes are operated under high loads, i.e. applying external bias voltages close to the open circuit voltage.

In this contribution we provide experimental evidence for a space charge limitation of the response time of organic photodiodes at bias voltages close to the open circuit voltage. The organization of the paper is as follows. After a brief description of the experimental procedures, we work out theory for describing the dynamical behavior of the bulk heterojunction photodiodes under open circuit conditions. Under illumination and at open circuit, the diode returns to its steady state with a relaxation time that is determined by the materials properties of the bulk heterojunction and the illumination intensity. Assuming that close to open circuit, currents in the diode are limited by space charge, we derive an explicit expression for this relaxation time and its dependence on illumination intensity. Subsequently, we present experimental

* Corresponding author.
E-mail address: s.c.j.meskers@tue.nl (S.C.J. Meskers).

http://dx.doi.org/10.1016/j.orgel.2016.04.032
1566-1199/

photo-impedance data and determine the relaxation time of the diodes under illumination and open circuit conditions. The experimental data confirm the theoretical predictions of the model for space charge limited photocurrent. Finally, we investigate the response time of the photodiode to small alterations in the light intensity and show that for bias voltages approaching the open circuit voltage, the response time converges asymptotically to the relaxation time determined from photo-impedance measurements. The results indicate that under the conditions chosen, the response time of the diodes is essentially determined by the type of carrier (electrons or holes) with the lowest mobility. Hence dynamical measurements on organic photovoltaic diodes can provide information on the mobility of the 'minority' charge carrier that cannot be accessed easily by static electrical current-voltage characteristics that are mainly determined by the type of charge carrier with the highest mobility.

2. Materials and methods

The diodes under study consist of a bulk heterojunction of poly [*N*-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) deposited from chlorobenzene solution with polymer: fullerene weight ratio of 1:4. The thickness of the bulk heterojunction was 300 nm. This thickness is suboptimal with respect to quantum efficiency but facilitates charge transport studies. Molybdenum oxide is used as anode and a LiF layer (3 nm) covered by a thin Al layer as semi-transparent cathode. Under AM1.5 like illumination conditions, the estimated photovoltaic power conversion efficiency amounts to 1%, with a fill factor of 0.3. Steady-state photocurrent–voltage (*J*-*V*) measurements were performed using a semiconductor analyzer and a continuous wave HeNe laser as light source (wavelength $\lambda = 543.5$ nm, maximum power density 125 mW/cm^2, beam diameter 1 mm). Light intensities were determined using a calibrated Si photodiode. The intensity of illumination was varied using calibrated neutral filters with optical density ranging from 0.16 to 4.08. Negative bias refers to the top LiF/Al contact being charged negative. Photoimpedance measurements under continuous illumination were done using a Solartron SI 1260 impedance analyzer. The amplitude of the ac voltage modulation was set to 10 mV. The response time of the organic photodiode (OPD) to small changes in illumination intensity was recorded under constant background illumination from the HeNe laser using modulated green light from a fast LED (Kingbright L-7104VGC-H green). The LED output was modulated into a triangular signal with a repetition frequency of 173 Hz using a function generator. The maximum intensity of the LED was 0.01 mW/cm^2, well below the intensity of the background illumination.

3. Theory

A photodiode under continuous illumination connected to an electric power source/sink is, in the thermodynamic sense, an open system out of equilibrium. In the limit of applying a very high external load to the diode under illumination, the diode is essentially operated under the open circuit condition. In this condition, it can be shown that the diode adopts a steady state [29]. After a small perturbation, the diode should return to its steady state with a characteristic time constant, the relaxation time, which is determined solely by diode parameters and independent of the external circuitry. Below we show that by considering the space charge limitation on the built-up of charge carriers in the diode under illumination, one can derive an expression for this relaxation time.

When the hole and electron mobility in a photodiode are unbalanced, e.g. $\mu_h << \mu_e$, then the charge carrier with the lowest mobility will accumulate near its extracting contact while the diode generates a photocurrent under illumination. This results in a space charge region that limits the photocurrent. According to Goodman and Rose [12] the photoconductance G_p is equal to:

$$G_p = qA\left(\frac{9\varepsilon_o\varepsilon_r\mu_h}{8q}\right)^{1/4} g^{3/4}V^{-1/2} \tag{1}$$

with q the elementary charge, A the active area of the diode, $\varepsilon_0\varepsilon_r$ the dielectric constant, and g the rate of charge carrier generation per unit volume. V is the potential difference over the space charge zone, which we assume to be equal to the difference between the externally applied bias V_{appl} and the open circuit voltage V_{oc} of the diode. The photocapacitance of the diode follows from the width of the space charge zone and equals [14]:

$$C_p = \varepsilon_0^{3/4}\varepsilon_r^{3/4}A\left(\frac{8qg}{9\mu_h}\right)^{3/4}(V)^{3/4}. \tag{2}$$

Under open circuit conditions, the relaxation time of the diode equals C_p/G_p, i.e. the RC time of the diode. Note that at open circuit, the external circuit puts an infinite load on the diode. Because the load and internal resistance are parallel, the total resistance of the diode and external circuitry equals the internal resistance of the diode under conditions close to open circuit. The relaxation time can be expressed as:

$$\tau = \left(\frac{8\varepsilon_0\varepsilon_r}{9\mu_h gq}\right)^{1/2} \tag{3}$$

We note that within this model, Eq. (3) can also be interpreted as the lifetime of the slowest charge carrier. Close to open circuit, the space charge limited relaxation time τ describes the characteristic time needed for internal redistribution of the accumulated minority carrier density when making infinitesimal changes in either light intensity or applied bias.

4. Results and discussion

Fig. 1 shows the *J*-*V* characteristics of the organic photodiode under illumination. In reverse bias at −2 V, the current density

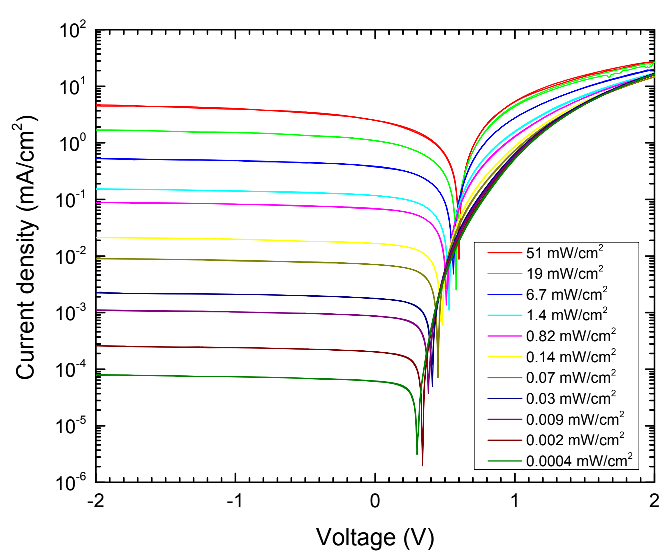

Fig. 1. Current-voltage characteristics of the organic photodiode as function of illumination intensity.