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Influence of bimolecular recombination on the photogeneration yield values determined by xerographic method

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ABSTRACT

Xerographic method consists in monitoring of decay of the surface potential of the photoconducting layer under illumination. The charge carrier photogeneration quantum yield is determined basing on the initial potential decay rate. In this work the photogeneration quantum yield for theoretically simulated initial surface potential decay is analyzed for a case when simultaneous photogeneration and recombination occur. A model disordered organic photoconductor is considered in which the photogeneration probability is described by the Onsager model of geminate recombination and the cross-section for recombination exhibits power dependence on the electric field. Photogeneration yields calculated in the classical way and the yields calculated with assumed bimolecular recombination are compared. It is shown that for high bimolecular recombination probability correctly determining the classical xerographic method of photogeneration quantum yield is difficult.

1. Introduction

Photogeneration in insulators or organic semiconductors is most often investigated by contact-less method called xerographic discharge (known also as surface potential decay technique) [1,2]. In this method a layer of the investigated semiconductor is deposited on metallic substrate, then it is charged in dark by means of corona discharge to desired potential and finally the decay of the surface potential induced by illumination is monitored. The rate of the surface potential decay, dV/dt, is proportional to the induced photocurrent which is dependent on photogeneration quantum yield but also on the not desired effects like formation of space charge [3–5], photoinjection [6–8], of charge carriers, trapping [7] and recombination [9–12] of electron–hole pairs. In the xerographic discharge method it is however possible to eliminate or at least to reduce most of these effects because:

- this is contact-less technique – layer of ions deposited on the free sample surface during the corona discharge forms the illuminated "electrode". Such ion layer is perfect blocking "electrode" therefore both dark- and photoinjection processes from the illuminated electrode are eliminated, for the illumination one can choose the light with wavelength corresponding to maximum of absorption of the investigated material. Such light will penetrate only very thin, surface layer of the photoconductor. Due to that photoinjection from the bottom, metallic electrode is negligible and also photogeneration of charge carriers in the bulk and formation of space charge is reduced. Such procedure, when applied to photoconductivity measurements with sandwich-type configuration would result in enhanced photoinjection from the front, illuminated electrode;
- the intensity of the light should be low and limited to the range in which the photocurrent is proportional to the photon flux. In such "small signal" regime the effects induced by large concentration of the photogenerated charge carriers should be negligibly small;
- the effects resulting from formation of space charge in the bulk by the photogenerated charge carriers moving towards the bottom electrode can be to great extent eliminated by limiting the analysis to the initial potential decay only, dV_0/dt at $t > 0$.

However, the above described procedure can be insufficient when the series of measurements for determination of photogeneration yield dependence upon the electric field intensity are carried out, what is needed to determine the mechanism of photogeneration. As the charge carrier mobility of one sign is essentially smaller than the mobility of the charge carriers of opposite sign, the "slower" charge carriers accumulate in the illuminated surface layer. These "slow" charges may be recombination centers or Coulombic traps for the opposite sign moving charge carriers resulting in the next photogeneration steps. In order to standardize the terminology we will now describe the meaning of the terms trapping and recombination, which will be used later in this article. Recombination centers are such places, in which occurs the total absorption of piece of the carrier opposite sign. Trap centers are those places where it is likely that the trapped charges

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can be (i) thermally excited and then take part in the flow of electric current or (ii) be absorbed by the recombination center. Trap centers, for which the probability of reemission of charge carries is much greater than the probability of recombination will be called traps, in the opposite case we are dealing with deep traps. According to the model, the recombination centers and deep Coulombic traps are bimolecular recombination centers. These phenomena results in increasing probability of bimolecular recombination during successive measurements. Effects caused by the charge carrier recombination are observed for a number of organic photoconductors [9–12].

In this work the analysis of the surface potential decay rate was performed for the model photoconductor with following properties:

(A) photogeneration creates mobile charge carriers (e.g. holes) while the charge carrier of opposite sign (e.g. electrons) are immobile and form recombination centers;
(B) trapping of the mobile charge carries in the volume of the photoconductor is negligible;
(C) the transport of the mobile charge carriers trough the sample is much faster than the rate of photogeneration (low illumination intensity and relatively high mobility);
(D) the potential decay occurs only when the sample is illuminated (no dark current);
(E) light is absorbed in a very thin layer of the photoconductor, close to the charged surface.

The equation describing the photodecay of the surface potential with the fulfillment of the above mentioned assumptions for the i discharging in the measurement series was discussed elsewhere and is given as follow [13]:

$$\frac{dV_{pi}(t)}{dt} = \varphi\eta(V_p)\left\{\sigma(V_p)[V_{pi}(0) - V_{pi}(t)] + \frac{Le}{\varepsilon\varepsilon_0}[\sigma(V_p)n_i(0) - 1]\right\} \quad (1)$$

where $V_{pi}(t)$ and $V_{pi}(0)$ are the surface potential and initial surface potential, $\sigma(V_p)$ is the electric field dependent cross section for recombination, $\eta(V_p)$ is the electric field dependent photogeneration quantum yield, φ is a number of absorbed photons per time unit and per area unit, L is the thickness of photoconducting layer, ε is dielectric constant, ε_0 is permittivity of free space, e is elementary charge, $n_i(0)$ is surface density of the recombination centers accumulated in the sample during the previous $i-1$ discharges and t is time.

The initial number of recombination centers $n_i(0)$ is described by the recurrent equation [13]:

$$n_i(0) = n_c + n_{i-1}(0) + \frac{\varepsilon\varepsilon_0}{Le}[V_{pi}(0) - V_{p(i-1)}(\infty)] \quad \text{for} \quad i \geq 2$$
$$\text{and} \quad n_1(0) = n_C \quad (2)$$

where n_c is the initial density of the recombination centers (which originates from photogeneration electron/hole pairs by light from the corona discharge), $V_{p(i-1)}(\infty)$ is the residual potential remaining in the sample after previous measurement (it is known from experiments, that even after long illumination the surface potential almost never falls to zero) [14,15].

With $dV_{p(i-1)}(t)/dt \to 0$ for $t \to \infty$, from Eq. (1) we have

$$\sigma(V_{p(i-1)}(\infty)) \cdot \left[V_{p(i-1)}(\infty) - V_{p(i-1)}(0) - \frac{Le}{\varepsilon\varepsilon_0}n_{(i-1)}(0)\right] + \frac{Le}{\varepsilon\varepsilon_0} = 0 \quad (3)$$

If the dependence of the active cross section for recombination on the electric field $\sigma(V_p)$, is known the recurrent set of Eqs. (2) and (3) gives the possibility to calculate the initial number of recombination centers $n_i(0)$ for i photodecay.

2. Formulation of the problem

According to classical approach, for any discharge in a series of subsequent measurements, if $n(0)\sigma(V_p(0)) \approx 0$ the recombination can be neglected and the photogeneration quantum yield η_{0i} is defined as (Eq. (1)):

$$\eta_{0i}(V_{pi}(0)) = -\frac{\varepsilon\varepsilon_0}{Le\varphi}\left.\frac{dV_{pi}(t)}{dt}\right|_{t=0} \quad (4)$$

Eq. (4) defines the way of photogeneration quantum yield determination by the classical xerographic method [2,16]. Using this approach the photogeneration for a number of organic photoconductors was investigated. It was found, that for not too strong electric field ($E < 10^6$ V/m), the photogeneration yield determined in this way decreases monotonically with a decrease of the surface potential [17–19]. This is in a disagreement with the theoretical photogeneration models (such as Onsager, Noolandi Hong, Braun, models) predict as well an existence of nonzero and independent of the electric field intensity photogeneration yield for the electric field $E \leq 10^6$ V/m [20–22].

The above described procedure of the photogeneration yield determination is based on an assumption that an influence of recombination and trapping on the rate of the potential decay in the initial instant can be ignored [16,18,19]. Two conditions must be however fulfilled:

c1 there is no trapping of charge carriers in the volume of the sample,
c2 there are no recombination centers in the area of photoconductor in which photogeneration takes place.

In order to reduce an influence of trapping on the initial rate of potential decay, the subsequent measurements are performed with time intervals long enough to liberate charge carriers from the deep traps [23].

Condition *c2* will be fulfilled when the lifetime of the recombination centers in the surface layer is short (it means when the probability of recombination with ions occurring on the photoconductor surface is high), so that during the intervals between the subsequent measurements the majority of the recombination centers will disappear.

In organic photoconductors usually only charge carriers of one sign contribute to the current flow [24]. They have several orders of magnitude higher mobility than charge carriers of opposite sign (in other words, the recombination centers are practically immobile). Therefore each subsequent experiment starts with higher and higher initial number of the recombination centers. The absolute cross-section for the recombination increases with each measurement and causes a reduction of the decay rate of the surface potential at $t = 0$, yielding apparently lower photogeneration yield. To avoid this effect in an analysis of the xerographic discharge the recombination phenomena must be taken into account and according to Eq. (1) the determined value of the photogeneration yield η_{Ri} would be

$$\eta_{Ri}(V_{pi}(0)) = \left.\frac{\varepsilon\varepsilon_0}{Le\varphi}\frac{dV_{pi}(t)}{dt}\right|_{t=0}[\sigma(V_{pi}(0))n_i(0) - 1]^{-1} \quad (5)$$

Let us consider the error arising when the data are analyzed without considering the recombination phenomena. We assume that the electric field dependence of the photogeneration yield is in an accordance with the photogeneration model based on the