Inhomogeneous bimolecular recombination in partially crystallised tri-methylphenyl diamine glasses

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ABSTRACT

The rise and fall dynamics of transient photocurrents induced by exposure to ultraviolet radiation have been analysed for a series of glassy tri-methylphenyl diamine films that have been partially crystallised by ageing under ambient conditions following vapour deposition. An inhomogeneous bimolecular recombination model that uses coupled rate equations is found to provide a consistent fit for the observed photocurrent dynamics provided the recombination rate of holes in the crystallised regions of the films is lower compared to the amorphous regions. Parameters returned by the bimolecular model are investigated as a function of the film age but are observed to be highly sensitive to the initial experimental estimates that are supplied for the effective hole recombination time. The effective hole recombination time generated by the model is found to be relatively independent of film age, however, and has a value of around 0.16 s for a carrier generation rate of 7×10^{14} cm^{-3} s^{-1}. The effective recombination time and steady-state photoconductivity magnitudes are found to be consistent with experimental hole mobility and photo-carrier generation efficiency values that are obtained using complementary time-of-flight and charge collection experiments.

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1. Introduction

Organic thin-film materials are increasingly being selected to provide key electronic functionality in a diverse range of commercial products in areas such as flexible displays, large-area imaging, and environmental sensing [1,2]. For many proposed opto-electronic applications, a benchmark parameter that is frequently used to validate the usefulness of an organic material is the mobility-lifetime (μτ) product of excess injected charge carriers. Although μτ magnitudes may be routinely extracted using standard photoconductivity techniques [3], it is often non-trivial to deduce the underlying recombination lifetime (τ), even if the mobility (μ) may be directly determined using time-of-flight methods. Recombination times that are calculated using independent μτ and mobility data are often found to show a significant difference to the rise and/or fall times observed under dynamic photoconductive testing [4]. An additional artefact that is sometimes observed during the photoconductive testing of thin-film materials is the apparent presence of fast and slow components in the dynamic photocurrent response. The presence of such components may indicate that the carrier recombination does not proceed in a homogeneous manner throughout the film bulk but is constrained to proceed via distinctive recombination channels that possess different recombination rates.

Bimolecular recombination between an electron population (n) and hole population (p) has been reported using photo-generation in single layer organic films [5], and using carrier injection from electrodes in multi-layer organic devices [6]. However, the evidence for bimolecular recombination from photoconductive studies is often principally based upon the required dependence of the steady-state photocurrent (I_{SS}) upon the volume generation rate (G) of carriers where $I_{SS} \propto G^{1/2}$ [3]. Comparatively few studies report upon the associated time (t) dynamics of the photocurrent which for homogeneous bimolecular recombination in the absence of trapping ($n = p$ everywhere throughout the material bulk) may be described using $dp/dt = G - Ap^2$ where A is the photo-carrier recombination rate. The solution of the homogeneous situation yields simple analytical expressions for both the rise ($I_R(t)$) and fall ($I_F(t)$) photocurrent responses where the recombination time $\tau = (GA)^{-1/2}$:

$$I_R(t) = I_{SS}\tanh(t/\tau) \tag{1a}$$

$$I_F(t) = I_{SS}[1 + (t/\tau)]^{-1} \tag{1b}$$

Failure to describe the photocurrent dynamics using a consistent parameter τ in the above expressions may then require that an alternative inhomogeneous recombination mechanism be considered. Pure inhomogeneous recombination may reflect underlying non-uniform bulk morphology and an interesting class of organic thin-film materials to study would accordingly be those which are prone to progressive crystallisation from an initial glassy state. The organic material selected for the present study was consequently *N,N′*-bis

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(3-methylphenyl)-N,N′-diphenylbenzidine (TPD) which may easily be vapour deposited as a thin amorphous film and which is then reported to slowly crystallise under ambient conditions in the presence of water vapour [7,8]. Photoconductive tests of partially crystallised TPD films were therefore examined for evidence of inhomogeneous recombination and the extraction of recombination parameters was attempted using coupled rate equations to model the bimolecular carrier dynamics. The recombination parameters that are returned using the proposed rate equation analysis are evaluated against TPD photoconductivity data in the literature.

2. Experimental details

The TPD material was sourced as a powder from a commercial supplier (Aldrich) and used without further purification. Thin films were deposited onto unheated glass substrates by vacuum evaporation from tungsten boats in an industrial coating unit (Edwards 306) at a base pressure of 3×10^{-3} Pa and deposition rates of about 30 nm s^{-1}. The deposited film thicknesses (d) were measured using a surface profilimeter (Dektak ST^3) and ranged from 0.2 to 1.2 μm for transient photo-conductivity (TPC) measurements, and from 6.0 to 7.1 μm for time-of-flight (TOF) and charge collection measurements. Newly deposited films appeared clear, uniform and transparent and were immediately fitted with the necessary metal electrodes to conduct the TPC and TOF work. For the TPC experiments, gold electrodes were deposited onto the surface of the thinner TPD films in a gap-cell configuration (width $W = 4$ mm, length $L = 1$ mm) to ensure that the necessary ohmic contact was achieved. To achieve the required blocking contacts for hole carriers in the TOF work, the thicker TPD films were sandwiched between aluminium electrodes to give an active device area of about 0.16 cm^2.

The TPC experiments were performed with a fixed voltage (V_A) of 500 V applied across the gap cell. An ultraviolet light-emitting-diode (LED) having a peak wavelength output at 380 nm was focussed onto the gap cell to photo-generate excess charge carriers. By controlling the LED current the total number of absorbed photons (N_{ph}) within the gap cell volume could be varied between 2×10^{18} cm^{-3} and 1×10^{20} cm^{-3}. The induced photocurrent signals were recorded on a digital oscilloscope in response to ignition and extinction events of the LED source. Using a proprietary current switch, the achievable ignition and extinction times for the LED emission were both less than 10 ms. The interval between ignition and extinction of the LED was chosen to be 10 s to ensure that a reference steady-state photocurrent I_{SS} was established. The induced TPC signals were typically averaged over four LED exposure events that were separated by an interval of about 30 s to ensure full recovery of the TPD films to the original dark equilibrium state following LED extinction.

A standard TOF arrangement [9] was used to perform mobility and charge collection measurements using the thicker TPD samples. Excess photo-carriers were generated using a 5 ns pulse from a nitrogen laser operating at 337 nm and transient signals were again recorded on a digital oscilloscope. For these measurements V_A was varied between 2 V and 200 V to allow the electric field dependence of the mobility and photo-generation efficiency (η) to be investigated.

All TPC and TOF experiments were conducted at room temperature (295 K) as the deposited films aged under dark ambient storage conditions over a period of up to 350 days. Visual monitoring of the films was performed using an optical microscope throughout the storage period and revealed the presence of small particulate regions. These particulates continued to grow in number and size as the films progressively aged as illustrated in Fig. 1. The observed evolution of film morphology is similar to that reported in independent studies of TPD film stability [8] where the formation of small crystalline regions within the as-deposited amorphous glass was detected using both optical and atomic force microscopy techniques.

3. Results and discussion

An example of the typical rise and fall transient photocurrent signals recorded for the TPD specimens is given in Fig. 2. The $I_R(t)$ signal (Fig. 2a) is initially observed to increase rapidly in response to the LED ignition but then slows noticeably before reaching I_{SS}. For the $I_F(t)$ signal (Fig. 2b) there is initially a rapid decay from I_{SS} in response to extinction of the LED which is then followed by a more leisurely approach towards zero photocurrent. The Fig. 2 signal behaviour is thus unlikely to be consistent with the homogeneous bimolecular recombination expressions given in Eqs. (1a) and (1b) which are characterised by a single recombination time parameter τ. This inconsistency is illustrated in Fig. 3 where the Fig. 2b fall signal is re-plotted as $I_{SS}/I_F(t)$ against t and fails to produce the linear response predicted by Eq. (1b) as $t \rightarrow 0$.

An alternative approach to model the recombination mechanism is to consider that bimolecular recombination occurs at essentially different recombination rates within the crystalline and amorphous regions of the TPD films. The physical justification for such a proposal is linked to the energy landscape that is generated by the localised alignment of TPD dipoles. Carrier transport through such dipolar landscapes is believed to proceed via a hopping mechanism and energetic barriers are anticipated to exist at crystalline–amorphous interfaces [10,11]. As TPD is a unipolar hole conductor, the photo-generation of electron–hole pairs will result in a population of mobile hole carriers (p), and a population of immobile electrons (n) that are distributed across crystalline (n_c) and amorphous (n_a) TPD sites. Bimolecular recombination between holes and electrons will therefore require the mobile holes to access both n_c and n_a type populations and this is likely to be harder in the former case due to the interfacial energy barriers. The associated recombination rates for the crystalline and amorphous regions may therefore be represented by distinct values A_c and A_a respectively where it is expected that $A_c < A_a$. If the volume concentration of crystalline to amorphous material is c_v, and the total bulk generation rate of electron–hole pairs upon photo-excitation is G, then it is possible to describe the overall dynamics of the mobile hole carriers (which are responsible for the ensuing photocurrent) by noting that $p(t) = n_c(t) + n_a(t)$ and then writing the appropriate rate equations for n_c and n_a. These rate equations may be expressed most compactly as:

$$\frac{dn_c}{dt} = G_c - A_c n_c (n_c + n_a) \quad (2a)$$

$$\frac{dn_a}{dt} = G_a - A_a n_a (n_c + n_a) \quad (2b)$$

In the above equations it is assumed that the local generation rate of electrons in the crystalline and amorphous regions are both proportional to their bulk volumes such that $G_c = c_v G$ and $G_a = (1 - c_v)G$. It is also implicitly assumed that there is no requirement to consider a spatial dependence for the hole population down through the film thickness due to the exponential absorption profile of the photo-excitation source. This simplifying assumption is expected to be valid provided the hole diffusion length is greater than the film thickness and will be discussed again later using recombination analysis data.

The coupled ordinary differential equations given in Eqs. (2a) and (2b) may be numerically solved to generate the rise and fall dynamics for $n_c(t)$ and $n_a(t)$ subject to the boundary conditions that are applicable to the TPC experiment. The solution procedure was verified by first comparing the numerical output against the analytical expressions of Eqs. (1a) and (1b) by setting $c_v = 1$ for the special case of homogeneous bimolecular recombination. For inhomogeneous situations where $c_v \neq 0$ the $I_R(t)$ response was generated by setting $n_c(0) = n_a(0) = 0$ and $G \neq 0$, and the $I_F(t)$ response by setting G =