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Fast transient photoconductivity in polydiacetylene: carrier photogeneration, carrier mobility and carrier recombination

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Abstract. We present a critical examination of the generation, recombination, and transport properties of the prototype one-dimensional photoconductor, PDA-TS. New sweepout measurements provide greater details of the temporal evolution of the photocurrent waveform. The data demonstrate that the carrier drift velocity is proportional to the external applied field in the time regime of less than 100 ns; the results yield a drift mobility of approximately 5 $cm^2 (V s)^{-1}$. We critically examine the previous studies of Donovan and Wilson and demonstrate by direct comparison with the experimental observations that the assumptions underlying their analysis of the data are not valid.

1. Introduction

In the last decade, considerable effort has been devoted to attempts to unravel the three generic aspects of transient photoconductivity: carrier photogeneration, carrier mobility, and carrier recombination processes [1]. Short laser pulses, matched microstripline configurations [2] and fast electronic detection systems have opened the subnanosecond to picosecond time domain and thereby facilitated the recent advances in this field. Utilising the resulting fast temporal resolution, experimental studies have revealed new information that has called into question concepts that were previously considered to be well established [3, 4].

In spite of this progress, there are major unresolved issues. In particular, the magnitude of the mobility in the prototype one-dimensional photoconductor polydiacetylene toluene-sulphonate (PDA-TS) and the role of geminate recombination in the same material continue to be controversial [3, 5–7]. The reported mobility in PDA-TS ranges over five orders of magnitude! Our purpose in this paper is to explore the source of the apparent controversy by a critical examination of the assumptions underlying the data analysis of the groups that have addressed this problem, and to provide new data that specifically address the unresolved issues.

A major problem is the magnitude of the mobility in PDA-TS in the time regime spanning a few hundred picoseconds after the pulsed photoexcitation. The contradictory conclusions arise fundamentally from the fact that the photoconductivity is a product of two variables: the number of photocarriers and their mobility. In the 'traditional' picture that is usually applied to conventional semiconductors, the quantum yield and mobility

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are independent of the applied electric field, so that the drift velocity and photocurrent increase linearly with field. On the other hand, both the quantum yield and the mobility can, in principle, be field dependent.

For PDA-TS, Donovan and Wilson have argued [5, 8] that the carrier quantum yield is linearly (or superlinearly) dependent on the applied electric field while the drift velocity is field independent even at fields as low as $E = 1\ \mathrm{V\ cm^{-1}}$. Their assumption has been that the only effect of the external field is to modify the carrier quantum yield through the field dependence which is anticipated as a fundamental feature of Onsager geminate recombination theory [9]. With this assumption, they estimated the mobility (at room temperature) to be $2 \times 10^5\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$, an ultra-high value; larger, in fact, that in any conventional semiconductor.

The peak photocurrent is proportional to the product of the carrier drift velocity $v_d = \mu E$ and the density of carriers $n = N\varphi\eta$ where N is the number of absorbed photons, φ is the initial quantum efficiency, and η is the probability of escaping geminate recombination. Hence, the experimental determination of both the carrier drift velocity and the carrier recombination mechanism solely from conventional transient photoconductivity measurements is a difficult problem. Direct experimental measurements of v_d are possible, however, if carrier sweepout can be achieved. Carrier sweepout has been achieved in PDA-TS; our results indicate that the carrier drift velocity increases approximately linearly in the applied field. From these measurements, a value for the mobility of $5\ \mathrm{cm^2\ (Vs)^{-1}}$ was deduced [3].

Early attempts to determine the quantum yield ($\varphi\eta$) utilised either steady-state photoconductivity [10, 11] or relatively 'slow' transient photoconductivity studies with modest temporal resolution ($t > 10$ ns) [5, 6, 8, 12]. More recent measurements [3] with sub-nanosecond resolution revealed an initial short-lived large photocurrent response followed by a 'tail' that extends over many orders of magnitude of time. Thus, the earlier data were dominated by the 'tail' and, as a result, provided no *direct* information of relevance to the photogeneration process (or to the question of geminate recombination). Our more recent measurements [3] with higher temporal resolution have shown that the magnitude of the initial photocurrent, its temperature dependence, and its electric field dependence are all inconsistent with the prediction of the Onsager geminate recombination theory, which previously has been extensively applied to PDA-TS [8, 10, 11].

In this paper we present a critical examination the generation, recombination, and transport properties of the prototype one-dimensional photoconductor, PDA-TS. We begin in the next section with a description of the results of carrier sweepout experiments which provide a direct measurement of the carrier mobility. New sweepout data with improved temporal resolution are presented which indicate in greater detail the evolution of the photocurrent waveform as the rate of carrier sweepout is increased at high bias fields. In § 3 we discuss the previous approach to data analysis and clarify the source of the apparent controversy. We show that the assumptions underlying the previous analysis are not valid, as demonstrated by direct comparison with the experimental observations. In § 4 we summarise the results and present a coherent picture of the generation, recombination and early transport in PDA-TS.

2. Experimental determination of the carrier mobility in PDA-TS

In order to unfold the complex phenomena of transient photoconductivity, it is essential to measure, independently, the drift velocity and the quantum yield. The fundamental questions that one would like to address are the following:

what is the effect of the applied field on the carrier drift velocity?
what is the magnitude of v_d?
what is the carrier photogeneration mechanism?

The carrier sweepout method has been the first, and to date the only, measurement that determines the magnitude of v_d and its field dependence in ns time regime. Recently, conventional time-of-flight measurements have extended the measurements of v_d into the time regime out to ~100 ns [13]. In the following, the results of both studies will be described and compared.

In order to understand the sweepout method, it is useful to first review the main features of the photocurrent response in PDA-TS and their implications. The waveform of the photocurrent indicates two distinct photoconduction processes [3]: the initial one is characterised by a fall time of about 300 ps; it is linearly dependent on the applied field as well as on the light intensity, I, and it is temperature independent. In contrast, the second photoconduction process (the photoconduction 'tail') was found to be strongly dependent on temperature; its magnitude is relatively high at room temperature and approaches zero as $T \rightarrow 0$. In contrast to the linear dependence of the initial response on I, the tail dependence on the light intensity is sublinear (proportional to $I^{0.74}$). For relatively short samples, of the order of a few μm, the photocurrent waveform is strongly dependent on E.

Carrier sweepout is attained when the velocity of the photogenerated carriers is such that they can be swept along the entire length (d) of the sample during a time interval that is equal to or less than the photocarrier lifetime. Non-ohmic contacts are required as well; the contacts need to be 'non-injecting' such that each carrier that reaches a contact is discharged without being replenished. Fortunately, gold in contact with PDA-TS constitutes a non-injecting contact [3] in the nanosecond regime. When these conditions are satisfied, the *shape of the waveform* of the photocurrent is expected to be field dependent only when the field modifies the drift velocity, v_d. The concept is quite fundamental. If an increase in the field leads to an increase in v_d, then as the field is increased the transit time, τ_{tr}, for the carriers to reach the contacts and be discharged is correspondingly decreased. As τ_{tr} becomes shorter, a larger fraction of the carriers reaches the contacts at shorter times, resulting in a more rapid decay of the photocurrent tail. Alternatively, if the field does not affect v_d, no change in the photocurent waveform would be anticipated. Hence, whether the sweepout effect is observed or not provides direct evidence of the dependence of the drift velocity on the applied field. It is important to note that the sweepout effect is expected to exist only when the sample length is of the order, or shorter than, the average distance travelled by a carrier before recombination; for a significantly larger sample, only a small fraction of the total photocarriers would reach the contacts and affect the rate of photocurrent decay. Therefore, the maximum sample length at which a sweepout effect is observed provides a rough measurement of the 'recombination length'.

Since in the stripline measuring configuration it is not possible to distinguish between the contribution of electrons and that of holes to the photocurrent, the term 'carriers' refers to both types of carriers. Therefore, the mobility of the thermalised carriers, as measured by the sweepout method, is the average mobility due to electrons and holes.

Our previous sweepout measurements were performed with a time window of about 3 ns; they yielded the field at which the photocurrent reached zero in samples of different lengths. Here we present a series of new results of sweepout measurements with higher temporal resolution performed on a single sample of 25 μm. The data directly illustrate the modification of the photocurent waveform as the external field is varied.

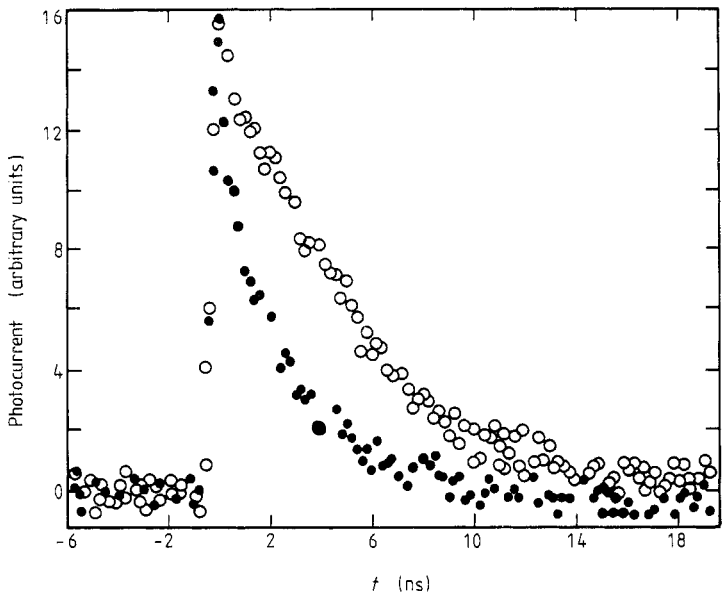

Figure 1. The effect of the applied electric field E on the photocurrent waveform in PDA-TS of a length of 25 μm. Plots are given for $E = 10$ V (○) and $E = 80$ V (●).

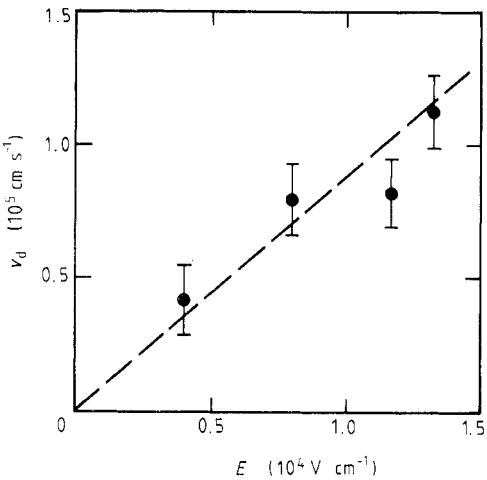

Figure 2. Field dependence of the drift velocity on the electric field.

As shown in figure 1, as the applied field is increased, the rate of decay of the photocurrent is increased, and the time at which the photocurrent reaches zero (which we define as the transit time, τ_{tr}) is decreased. The carrier drift velocity, $v_d = d/(2\tau_{tr})$, as a function of the applied field is shown in figure 2. An approximately linear dependence of v_d on E is obtained. The observed dependence of the photocurrent on E is unambiguously identified as due to carrier sweepout, since it is exclusively observed in relatively short samples of the order of 10–25 μm. In samples with $d = 200$ μm no such effects were observed. (We point out that the conclusion that the drift velocity varies with the applied field has been recently reached by two other groups that have used a different experimental approach [12, 14].)

Recent conventional time-of-flight studies PDA-TS by Donovan *et al* [13] provide complementary information on the drift velocity at times $t > 100$ ns. In these experiments, photogenerated carriers in a narrow region at one side of the sample are swept across the entire length of the sample (length between 250 μm and 1000 μm). Transit times are several hundred ns. Their data indicate that the drift velocity is an approximately linear function of the applied field and that the mobility is about 1 $cm^2 (Vs)^{-1}$. This value of the mobility at time $t > 100$ ns is consistent with our measured mobility of 5 cm^2/Vs at 4 ns, since at this time regime the photoconductivity (as exhibited by the tail) is dominated by a trap limited mobility. As time progresses the photocarriers are trapped by progressively deeper trap energy levels; thus the photocarrier mobility is expected to be a monotonically decreasing function of time as the rate of carrier release from these traps is correspondingly decreased.

3. Analysis of previous studies of the mobility in PDA-TS

We begin with a discussion of the main results of the work of Donovan and Wilson [5, 6, 8]. Their analysis of PDA-TS is based on the expressions for the photocurrent, I_p, and the total charge Q_m transferred to the electrodes as a result of the photocurrent created by a single laser pulse:

$$I_p(t) = e\eta\varphi N n(t) v_d(t)/d \tag{1}$$

where e is the carrier charge, φ is the quantum efficiency for carrier pair creation, η is the probability that the pair will escape geminate recombination, N is the total number of photons absorbed, v_d is the time-dependent drift velocity, and d is the electrode separation. In equation (1), $n(t)$ is the (normalised) bulk carrier recombination function; $n(0) = 1$, and $n(t)$ decreases monotonically to zero as $t \to \infty$. If carrier recombination occurs only at the electrodes $n(t) = 1$, and equation (1) can be integrated:

$$Q_m = e\eta\varphi N s/d \tag{2}$$

where s is the mean distance travelled by the carrier. Donovan and Wilson claim that bulk recombination is negligible and that *all* the photogenerated carriers which escape geminate recombination reach the contacts; i.e. $s = d$. With this assumptions, they obtain

$$I_p(t)/Q_m = v_d(t)/d \tag{3}$$

which yields the drift velocity as a function of time. According to equation (3), in the absence of bulk recombination the decay of the photocurent is determined solely by the time variation of the drift velocity. Furthermore, Donovan and Wilson [5, 15] have concluded that the characteristic carrier trapping time is 500 ns, and that the traps are 1100 μm apart on a chain; thus, they have concluded that during this time (about 500 ns) the drift velocity is constant ($v_d = 2 \times 10^5$ cm s^{-1}). However, these conclusions are in major contradiction with the observation that I_p decreases by at least three orders of magnitude during the time before trapping [3]. This implies that the assumption of negligible bulk recombination is seriously violated; the observed variation of the I_p as well as the observation of the mobility being of the order of few $cm^2(Vs)^{-1}$ in the time regime of 500 ns imply that $n(t)$ in fact decreases by about three orders of magnitude in this time interval.

Equation (3) does not take into account carrier recombination at the contacts due to carriers that are photoexcited in proximity to the contacts, and that may reach the

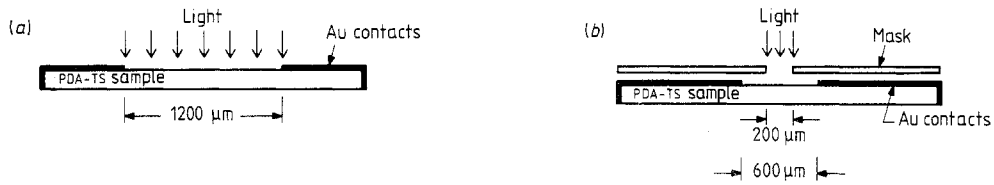

Figure 3. The measuring configurations that were used in order to minimise carrier recombination at the contacts: (*a*) relatively long sample of length $d = 1200$ μm that was uniformly illuminated, and (*b*) sample of length 600 μm that was illuminated by the pulsed laser only at the middle 200 μm, leaving the two masked regions close to the electrodes unilluminated.

electrodes at a time t. In order to experimentally realise a condition where carrier recombination at the contacts is negligible, the photocurrent waveform was measured in two special configurations that are shown schematically in figure 3: (*a*) in a relatively long sample of $d = 1200$ μm, and (*b*) in a sample of a length of $d = 600$ μm that was illuminated by the pulsed laser only at the middle 200 μm, leaving the two masked regions close to the electrodes (of width of 200 μm, each) unilluminated. In the first configuration only about 16% of the photoexcited carriers could have reached the contacts during a time of 100 ns (assuming $v_d = 2 \times 10^5$ cm s^{-1}), while in the second configuration effectively none of the photoexcited carriers in the middle of the sample could have reached the contact during a time of 100 ns. However, in both configurations the observed photocurrent waveform exhibited rapidly and monotonously decreasing I_p as a function of time, identical to the previously observed waveform in the experiments where the entire sample (of 200 μm) was illuminated. Thus, again, we conclude that bulk recombination (and trapping) exist at all observed time scales after carrier photogeneration.

Direct evidence of the importance of recombination is also obtained from the sweepout studies. As noted in § 2, sweepout has been observed exclusively in samples with length d less than 25 μm. Only for such lengths does a significant fraction of the carriers reach the contacts. For $d = 200$ μm, sweepout was not detected, indicating that indeed only a small fraction of the carriers reach the contacts. The sweepout measurement provides a rough measurement of the typical distance, s, that a carrier propagates before recombination; for $e = 10^4$ V cm^{-1}, s is about 10 μm, which is significantly smaller than assumed previously (up to a few mm) [5, 15], and inconsistent with the assumption that $s = d$. At longer times the photocurrent is further reduced by recombination; nevertheless, by looking carefully at the residual small photocurrent, Donovan, Fisher and Wilson were able to detect the time-of-flight signature at ~400 ns, and thereby obtain the mobility [13]. That they obtained a value in general agreement with that obtained by sweepout at a few ns demonstrates independently that the mobility is approximately constant with a value of a few cm^2 (V s)$^{-1}$ over the entire time domain (from sub-nanosecond to hundreds of ns), and that the current decay is caused predominantly by recombination.

Bulk recombination in PDA-TS has been recently observed by Frankevich *et al* [14]. These investigators have studied the steady-state photoconductivity in samples of various lengths (or the order of 1000 μm) and found that the photocurrent is independent of the sample length (for identical density of absorbed photons as well as applied field). Thus, they have concluded that the carrier lifetime is dominated by the bulk recombination rather than by the carrier transit time to the contacts, in agreement with our conclusion.

Donovan and Wilson have assumed that the trapping time (i.e. the average time before carrier is first trapped) is the source of the decay in photocurrent at times less

than few hundred ns [5, 8, 15]. They argued that the drastically lower mobility (by five orders of magnitude) after about 100 ns is due to the carrier release from traps (by a field assisted mechanism) as the limiting process. however, both the sweepout results (times of order a few ns) and the time-of-flight experiments (times of order a few hundred ns) yield consistent results for the mobility with magnitude of the order of a few $cm^2 (V\,s)^{-1}$. Therefore, based upon direct measurements of the carrier mobility there is no evidence of the proposed five order of magnitude difference in mobility. Moreover, the observation that the mobility is approximately constant over the entire time domain (subnanosecond to hundreds of ns) with a value of a few $cm^2 (V\,s)^{-1}$ implies that the initial trapping time is in the picosecond regime and that the measured mobility is trap limited over this entire time domain, a conclusion that has been reached previously by Blum and Bassler [12].

Assuming negligible carrier recombination the derivations for I_p and Q_m (equations (1) and (2)) predict that both quantities are linearly proportional to the light intensity (i.e. the number of absorbed photons). However, the experimental results indicate that these quantities have markedly different dependencies on light intensity and temperature; I_p is found to be linearly dependent on light intensity, I, while Q_m varies as $I^{0.74}$. This again implies that excessive recombination must take place during the decay of the initial photocurrent response. As the intensity is increased, a higher density of photoinjected carriers is created, and I_p increases correspondingly. However, the excessive recombination at higher intensities results in a smaller number of surviving carriers; hence the sublinear dependence of Q_m on I. Excessive trapping at low temperatures limits even more the extent to which the carriers propagate, which in turn affects the measured Q_m independently of the subnanosecond carrier drift velocity at that temperature. Thus, these observations indicate that the assumption of negligible carrier recombination is not valid.

The tail of the photoconductivity signal disappears as $T \rightarrow 0$. Since the thermally activated carrier release process becomes exceedingly long as $T \rightarrow 0$, once a carrier is trapped it is not released back to the conduction band (for electrons, or valence band for holes). This is also the reason why the observed steady-state photoconductivity is an exponentially decreasing function of the temperature, in contrast to the temperature-independent initial photoconduction response. The disappearance of the tail at low temperatures indicates that the trapping time must be smaller than 300 ps, which is a much shorter time than that assumed by Donovan and Wilson (>50 ns) [15].

The peak photocurrent I_p and the integrated charge Q_m were found to have the same dependence on the field E (roughly linear). This was used as confirmation that the drift velocity is independent of the field (the field dependence being in η). However, the field independence of the ratio I_p/Q_m certainly does not imply the field independence of v_d. Since the typical distance a carrier propagates before recombination is much smaller than the sample length, the total charge that reaches the contacts depends on the drift velocity; the higher v_d the higher the number of carriers that reach the contacts. In this case both the photocurrent I_p and its time integral Q_m would have similar dependences on $v_d(E)$, and the ratio of (3) would be field independent.

Donovan and Wilson have recently improved the temporal resolution of their measurements through implementation of the Auston switch measuring technique [7]. In agreement with our results [3], they found the initial response to be roughly temperature independent, in contrast to the strong temperature dependence that they observed previously [5, 8]. As a result of these data, they modified their previous interpretation of the carrier photogeneration mechanism in PDA-TS [7]. They attributed the short-lived

initial photocurrent to a relatively small number of photogenerated hot carriers, while the majority of the photocarriers were assumed to be created with lower energy, within the Coulomb potential well of the geminate carrier partner. Thus, the photogeneration mechanism of the majority of the carriers was assumed to exhibit the field and temperature dependences of the Onsager theory. This assertion is, however, not in agreement with the observation of the temperature independence of both the magnitude of the initial photocurrent response and its rate of decay (about 300 ps). If the photogeneration mechanism of the majority of the carriers were as predicted by Onsager theory, it would have dominated the initial photocurrent, and in particular, would have exhibited a decreasing photocurrent as the sample temperature approaches zero, in contrast to observation.

Donovan and Wilson provided an analysis of the Auston switch configuration which suggested that the carrier sweepout effect should not exist [7]. In their analysis of the equipotential lines and the resulting current path it seems that they considered only the top stripline conductor and ignored the adjacent zero potential (ground) line in the stripline configuration. A solution of the actual Auston switch electrode geometry can be obtained by transforming to an equivalent geometry with an isotropic sample (all lengths scale as the square root of the conductivity ratio). In particular, for the magnitude of the anisotropy of PDA-TS, the effective length of the sample is close to the length of the gap in the stripline conductor. The carrier path length may vary with the depth below the illuminated surface at which the carrier is photogenerated; this may influence to some extent the shape of the photocurrent waveform. However, regardless of this variation of carrier path length, in short samples carriers can reach the contacts before they recombine at the sample. Thus, as the drift velocity increases at higher applied field, the carrier transit time decreases, resulting in an enhancement of the rate of recombination at the contacts and a more rapid decay of the photocurrent, as indeed the sweepout measurements indicate.

Finally, we note that the existence of two distinct photoconduction mechanisms as well as the observation of fast recombination and trapping at extremely short timescales implies that the measurement of the quantum yield on the basis of steady-state photoconductivity [10] is not a valid experimental approach. Generally, the steady-state photocurrent response is dependent on the photoconduction at all timescales after photoexcitation. Since the 'time window' in these experiments is extremely long compared to the lifetime of the initial photoconduction mechanism, the photocurrent response is dominated by the second, long-lived, trap-limited transport mechanism. Thus, the steady-state photocurrent response is severely affected by recombination as well as the lower mobility at relatively long times after carrier photogeneration (as carriers sink to progressively deeper trap levels). Therefore, adequate investigation of the carrier photogeneration can be addressed only with sufficient experimental temporal resolution to resolve the short-lived initial transient photoconduction response (in PDA-TS, this initial response persists only about 300 ps).

4. Carrier photogeneration mechanism in PDA-TS

For many years, the accepted notion has been that for the class of low-mobility photoconductors, the carrier quantum yield from photoexcitation is low and is dependent on the probability of a carrier escaping geminate recombination [1]. Numerous studies, e.g. in anthracene [16] and amorphous selenium [17] have led to the acceptance of

the validity of the Onsager theory of geminate recombination. This theory has been extensively applied also to PDA-TS. However, as the results of transient photoconductivity experiments with higher temporal resolution have become available for PDA-TS, it has become clear that the behaviour of I_p at short times is different from that previously observed with relatively poor temporal resolution [5, 8, 18]. The initial photocurrent response observed in our measurements [3] does not conform with the prediction of the Onsager theory; it was found to be temperature independent in contrast to the theoretical prediction of an exponential dependence (with $1/T$). The previous transient photoconductivity studies [18] in PDA-TS with time resolution of $t > 10$ ns reported a peak response that strongly varied with temperature in the region 80 K to 300 K, and remains roughly temperature independent below 80 K. However, we now know that in these measurements the temperature dependence at $T > 80$ K was dominated by the 'tail', which (in contrast to the initial peak) is indeed strongly temperature dependent. Below about 80 K the magnitude of the tail is exceedingly small; thus, although the integration time of the experimental system was about 10 ns, the freeze-out of the contribution of the 'tail' dominated the temperature independence of I_p at $T < 80$ K. Although the early results were modelled in terms of Onsager geminate recombination theory, the existence of the temperature-independent initial response as observed in higher temporal resolution measurements, demonstrates that the photocarriers must be generated by a different process.

The observed temperature independence of the (unresolved) peak photocurrent [3] of PDA-TS has led to the conclusion that photoexcitation results in the initial generation of hot carriers. Promptly after the carrier photogeneration three processes become operative:

(i) carrier thermalisation
(ii) recombination
(iii) trapping

where each process may dominate within a different time regime.

Carrier thermalisation and recombination. We have suggested that the relatively high quantum yield (10^{-3} at 4 ns) may be due to the initial hot carrier motion which results in a higher probability of the carrier escaping the Coulomb geminate potential well. During the initial carrier thermalisation (of electrons in the conduction band and holes in the valence band) the recombination rate is expected to be high since the density of carriers is maximum. The magnitude of peak photoconductive response is characterised by the hot carrier mobility and the recombination during the integration time of the measuring system. Recombination occurs at all timescales ranging from the initial (unresolved) response all the way out to the tail.

Trapping. From our measurements, the time for carrier localisation into traps appears to be quite rapid; certainly the decrease in the tail at low temperatures suggests complete trapping after a few hundred picoseconds. It is plausible that carrier trapping begins at the end of the initial ballistic motion, and becomes particularly significant after the completion of carrier thermalisation into the bottom of the conduction band. The mobility is, therefore, expected to be a function of time; it is a maximum during the initial ballistic motion, and it decreases continuously as time progresses. Trap-limited mobility certainly dominates the carrier motion at all times beyond a few hundred picoseconds; as time progresses, carriers are trapped by successively deeper trap levels

that further reduce the mobility. In our view, after about 300 ps, trap-limited transport (with concurrent recombination) is the only operative transport mechanism.

The mechanism that we have suggested is based on the photogeneration of hot carriers. The acquired excess energy, $E > k_B T$, of the hot carriers is due either to the difference between the photon excitation energy and the band energy gap or due to a ballistic acceleration of the carriers by the external field prior to the first trapping or scattering event. The initial ballistic motion should be distinguished from a carrier diffusion motion (assumed in the Onsager theory), as is evident from the employment of the Einstein relation for the mobility in that theory. The observation of temperature-independent I_p also excludes the possibility of the coexistence of two carrier photogeneration mechanisms, the classical Onsager theory and a second temperature-independent mechanism, since in this case some temperature dependence of I_p would have remained due to that fraction of carriers that behave according to the expectation of the Onsager theory.

5. Conclusion

In summary, new sweepout measurements with better time resolution demonstrate that the carrier drift velocity is proportional to the external applied field in the time regime $t < 100$ ns. These observations are in complete agreement with our previous measurements as well as with the time-of-flight studies and indicate a mobility of approximately 5 $cm^2 (V\ s)^{-1}$. The experimental observations of temperature-independent carrier quantum yield and the field dependence of the drift velocity indicate the breakdown of the Onsager geminate recombination theory, and the need for an alternative mechanism for describing the carrier generation process. We have discussed the previous data analysis that resulted in the claim of an ultra-high mobility. We found that the basic assumptions that have been made are inconsistent with direct experimental observations; in particular the assumption that there is no significant recombination during the relevant time period after photoexcitation (up to a few hundred ns) is not valid.

It was recently observed that the features which characterise the breakdown of the Onsager theory of geminate recombination in PDA-TS are observed in a whole class of low-mobility photoconductors. Studies of fast transient photoconductivity in single crystal anthracene [4] as well in amorphous selenium [4], both of which have been considered prototype systems that demonstrate the validity of the Onsager geminate theory, have shown the same general features: the existence of two distinct photoconduction mechanisms as well as the relatively large and temperature-independent quantum yield. It seems that the effective separation of the geminate carriers beyond the Coulomb capture distance due to photogenerated hot carriers may be a general feature of the carrier photogeneration mechanism in low-mobility materials. The existence of short-lived initial photoconductive response in low-mobility materials (that may extend in amorphous semiconductors to only a few tens of ps, or less) requires that high experimental temporal resolution be used. The crucial importance of this requirement has now been clearly demonstrated for PDA-TS.

Acknowledgments

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