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The effect of electric field on the bimolecular recombination rate in a one-dimensional polymer single crystal

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Abstract. This work presents results which demonstrate that, for a one-dimensional semiconducting system, an applied electric field can affect the rate at which photocreated carriers bimolecularly recombine. Such an effect would not be expected in three-dimensional materials. The effect in the one-dimensional single crystal polydiacetylenes has led to previous workers making errors of interpretation of their observations. This present work seeks to correct these, and demonstrate that all observations are consistent with the view that carriers move with a saturated drift velocity, at around the velocity of sound, characteristic of the motion of a solitary wave acoustic polaron in one dimension. Furthermore, the field dependence of the bimolecular recombination rate is seen to be a direct consequence of the Onsager geminate recombination mechanism, as modified to account for the one dimensionality of the semiconductor.

1. Introduction

Certain diacetylene single crystals polymerise in the solid state to form highly perfect macroscopic single crystals of polydiacetylene (PDA). Such conjugated polymer single crystals have excited much interest in particularly because of their electronic properties as they provide a highly anisotropic, quasi 1D semiconducting system. That is, the chains are covalently bonded along the chain direction but individual chains in the crystal are held some distance apart by Van der Waals forces, their separation determined by the side group attached to the diacetylene. Thus, electron overlap is strong along the chain, and motion of a free carrier may be expected to take place in a conduction band. Perpendicular to the chains, however, motion is controlled by rare interchain hops. This one dimensionality is demonstrated in the highly anisotropic dark conductivity, where $\sigma_{\parallel}/\sigma_{\perp} = 900$ (Siddiqui and Wilson, 1979).

The most widely studied of these PDAs is the toluene sulphonate derivative, PDA TS, as it forms the best macroscopic single crystals. It is a semiconductor with a band gap of 2.4 eV. The study of the motion of excess carriers photocreated across the band gap with pulsed laser light has led the group at QMW to conclude that the carriers move with a drift velocity that is independent of electric field down to fields as low as 10^2 V m^{-1} and that the saturated drift velocity is that of the sound velocity, $v_d = 2.2 \times 10^3$ m s^{-1}. This entails an ultra high low-field mobility, $\mu > 2.2 \times 10^5$ m^2 V^{-1} s^{-1} (Donovan and Wilson

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1981a). This conclusion has been re-enforced by a large number of experimental studies (Donovan *et al* 1985, Donovan and Wilson 1990). Furthermore, it is now understood theoretically to be the expected motion of an excess carrier in one dimension, where that carrier will create an acoustic deformation of the polymer chain, irrespective of the magnitude of the electron–phonon coupling (provided it is non-zero) thereby lowering its energy. The composite object is a solitary wave acoustic polaron, SWAP, which when pulled by an external electric field takes the deformation with it. It is the acoustic deformation that limits the velocity of the SWAP to the velocity of sound. Because a single phonon process will not suffice to scatter the SWAP while conserving energy and momentum, the high low-field mobility results (Wilson 1983, Gogolin 1988). The SWAP has been described theoretically, and its stability demonstrated with the respect to formation of other quasi-particles (Wilson 1989). The SWAP has also been computer simulated and the predicted properties observed (Wilson private communication). Nevertheless, this is still the object of some controversy. Recent work by Moses and Heeger (1989) claims to have demonstrated that the drift velocity is linear in electric field. Using an Auston switch electrode geometry with a narrow gap they observe, with increasing electric field, a more rapidly decaying photocurrent. This, then, is attributed to the fact that as the field is increased the drift velocity rises, the carriers are thus swept out from the gap more rapidly and the carrier decay rate increases accordingly. Were the observation and its interpretation indeed correct, the existence of the SWAP would be called into question. The experiments described in this paper show that, while their observations were correct, they were incomplete, and their interpretation as a consequence in error. We are now able to offer an explanation for all experimental observations by all groups within one framework.

It is almost universally accepted that the photogeneration rate for free carrier pair production in one dimension is field dependent. This reflects the probability that a thermalized electron–hole pair will, in zero applied field, definitely geminately recombine in 1D (Donovan and Wilson 1981b, Seiferfeld *et al* 1983). The application of an external field increases the probability that the thermalized pair escape this eventuality and survive as separated carriers able to contribute to the photocurrent. The process is well described by the Onsager theory of geminate recombination as modified to 1D (Blossey 1974, Haberkorn and Michelle-Beyerle 1973, Wilson 1980). The probability, $\varphi(E)$, that a carrier pair will separate is linear in electric field, E, at low fields, becoming superlinear above a critical field of around 10^5 V m^{-1}. Hence by increasing the electric field the electron and hole densities, $n = p$, are increased. When these densities are high enough, the rate of decay of the photocurrent is determined by bimolecular recombination with a characteristic time given by $(\beta n)^{-1}$, where β is the bimolecular recombination coefficient. Because increasing E brings about an increase in n, the decay time decreases correspondingly. It is shown in this work that it is precisely this effect that was previously ascribed erroneously to sweep out and a drift velocity linear in field.

2. Experimental

Single-crystal PDA TS with surface electrodes in the form of a 50 Ω stripline with a 6.5 μm gap, forming a photoconductive Auston switch, was used. Voltage was applied to one side of the gap and the configuration produces a complicated field whose largest component is in the chain direction (Donovan and Wilson 1989). The other side was connected to a boxcar sampling system with 75 ps gate width. With light incident on the

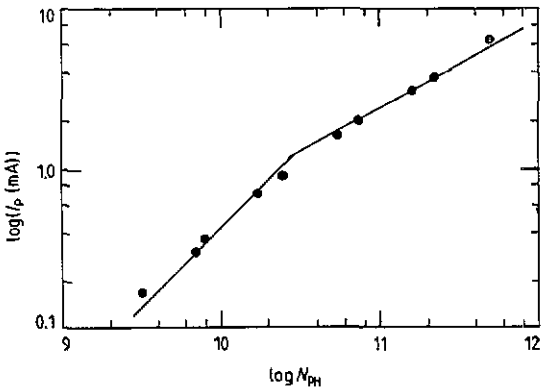

Figure 1. Photocurrent, I_P, due to absorption of photons, N_{PH}, within an Auston switch gap of 6.5 μm, at an applied voltage of 20 V.

gap a fast photocurrent was measured. 50 Ω coaxial cable and termination was used throughout to maintain signal integrity. The frequency tripled output of a mode locked Nd YAG laser was used to excite the photocurrent, the pulse width being 25 ps and photon energy 3.5 eV. Use of the fast boxcar acquisition system required many laser pulses to build up a current decay point by point and to average out noise to an acceptable level. Because the electrodes are non-injecting, and due to the presence of some deep trapping centres, care was taken to avoid space charge build up during data acquisition. This was achieved by switching on the applied voltage for 500 μs and firing the laser in the middle of the voltage pulse. The subsequent two laser shots were fired with zero volts across the sample to clear space charge. By multiplexing, data taken with the field applied was collected in one curve and data taken with zero applied field in a second curve. In this way, sample charging and reduction of the applied field was avoided during data collection. It was important to know the light energy falling on the sample gap. This was achieved by focusing the light to a line of 75 μm width on the sample. A reticon was used to measure the width of the focused beam. By using a beam splitter, it was possible to take a small amount of the light to the reticon CCD array, which was carefully positioned in an equivalent focal plane to that of the sample, thus ensuring reasonably accurate knowledge of the beam width at the sample. An energy monitor placed at the sample position at the beginning and end of data collection measured the total energy in the focused beam, and the energy on the sample was thus found using appropriate geometric factors. With this care the absolute light intensity at the sample could be known to within an accuracy of 60%. The main source of error was the resolution of the reticon which was 25 μm. Relative light intensities are known to a far greater accuracy.

3. Results

Figure 1 shows the dependence of the peak photocurrent, I_P, on N_{PH}, the number of photons absorbed in the gap at a constant applied voltage. This dependence shows a linear varition of I_P with N_{PH} going over to a $\sqrt{N_{PH}}$ dependence as N_{PH} is increased and the current exceeds 1 mA. This usually signifies a change of carrier loss mechanism going from a linear, trapping, transiting, or Shockley–Read recombination mechanism with

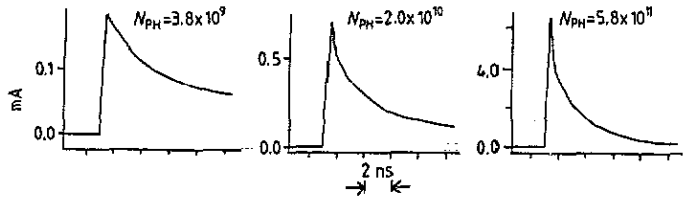

Figure 2. The photocurrent with 20 V applied as the number of photons absorbed, N_{PH}, increases.

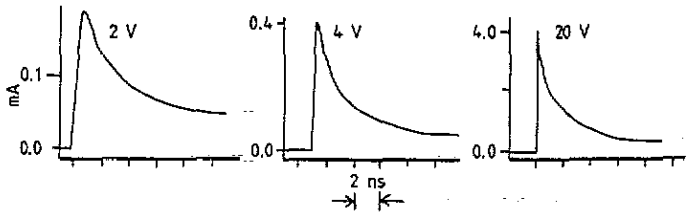

Figure 3. The photocurrent with constant number of photons absorbed, $N_{PH} = 2.9 \times 10^{11}$, as voltage increases.

characteristic trapping time τ, to a bimolecular recombination regime where the characteristic carrier loss time is $(\beta n)^{-1}$, with β the bimolecular recombination rate. That the bimolecular regime is observed in measurements of the pulse height means that the recombination time, $(\beta n)^{-1}$, is equal to or less than the laser pulse width, $T_L = 25$ ps. Figure 2 shows a collection of photocurrent decays taken at constant electric field with light intensity increased from left to right. The increase in decay rate with increasing intensity is as expected for the bimolecular regime as evidenced by the $\sqrt{N_{PH}}$ dependence of I_P. Figure 3 shows a collection of curves where the light intensity is held constant and the field is increased from left to right, and the decay rate is seen to increase as the field increases. This is the measurement others have erroneously associated with carrier sweep out. Figures 2 and 3 mirror each other and demonstrate that the only quantity of importance in determining the decay rate is the peak amplitude, I_P, of the photocurrent.

Figure 4 shows the field dependence of I_P. Once again there is a change to a weaker dependence on field above a current of 1 mA, a situation exactly paralleled in the intensity dependence of figure 1.

4. Discussion

Figures 1 and 2 demonstrate clearly that bimolecular recombination is the dominant carrier decay mode at signal levels above 1 mA. Given the electrode width, w, of 1.2 mm, and the absorption skin depth, $\delta = 0.7\ \mu$m for the excitation wavelength used, this corresponds to a current density of 1.2×10^2 A cm^{-2}. Current levels greater than this cause bimolecular recombination to occur on a time scale faster than that in which I_p is created, $T_L = 25$ ps. These results may be analyzed within a simple framework to deduce the bimolecular recombination cross section, σ, in PDA TS, as follows.

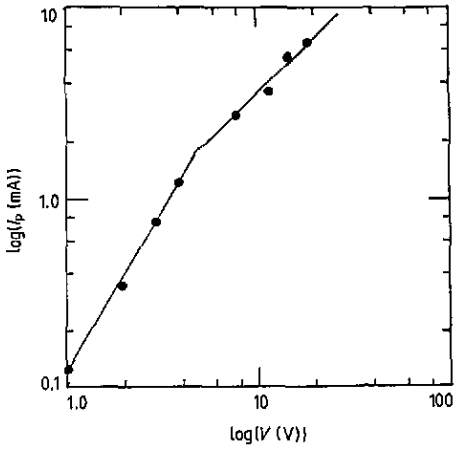

Figure 4. The voltage dependence of the peak photocurrent, I_P, at constant photon absorption, $N_{PH} = 5.8 \times 10^{11}$.

At a critical current I_C the carrier density reaches a critical value n_c such that $\beta n_C = T_L^{-1}$ and above this value of carrier density the peak current varies as $\sqrt{N_{PH}}$. From figure 1 we may identify $I_C = 1.0$ mA. The peak current in the linear regime is

$$I_P = nevw\delta \tag{1}$$

and

$$I_C = n_C evw\delta. \tag{2}$$

Therefore

$$\beta = 1/T_L n_C = evw\delta/I_C T_L. \tag{3}$$

Here v is the carrier velocity. Furthermore, if we treat the recombination as a one-dimensional process, we can write

$$\beta = \sigma v. \tag{4}$$

Combining equations (3) and (4) we have an expression for σ:

$$\sigma = ew\delta/I_C T_L. \tag{5}$$

In this expression all the quantities on the right are known:

$T_L = 25$ ps $\quad I_C = 1.0$ mA $\quad w = 1.2$ mm $\quad \delta = 0.7\ \mu$m $\quad e = 1.6 \times 10^{-19}$

and so we deduce the capture cross section $\sigma = 5.37 \times 10^{-15}$ m^2. Thus the recombination capture radius $r_C = 41$ nm.

It is to be noted that in this analysis no assumptions were made as to the value of the drift velocity, and an absolute measurement of the light intensity was not required. The only assumption was that the velocity of equation (4) is the same as that of equation (2). This is a one-dimensional argument, for in 3D, in equation (4) a thermal velocity would be used, while for equation (2) the carrier drift velocity is still appropriate. If the motion is purely one dimensional an electron drifts on a chain until it encounters a hole within its Coulomb sphere of interaction, whereupon it will recombine.

The Coulomb radius expected for carriers to have binding energy kT at room temperature in PDATS, using a dielectric constant, $\varepsilon = 3.24$, is given by: $r_{kT} = e^2/4\pi\varepsilon\varepsilon_0 kT = 17.2$ nm.

The value of the capture radius deduced from the simple model given above is then in remarkable agreement with the value expected from theoretical considerations.

An interesting possibility is that bimolecular recombination can occur when there are fewer than one carrier pair per chain. What is observed is a pseudo recombination, where a hole arrests the motion of an electron on a chain up to 60 chains away, within r_c, and this appears to the experimentalist working at short times as true recombination with all the characteristic signs. However the carrier pair have not annihilated, as interchain hopping is rare, and they may subsequently become free of each other and once again contribute to the photocurrent in the longer term. This is more true for those pairs captured at greater distances. The experimentalist working at longer times will be unaware of the occurrence of this encounter. This would be a uniquely one-dimensional phenomenon and it requires further investigation.

Another unique observation of these results is the effect of electric field on bimolecular recombination rates through the strongly field-dependent carrier generation rate. This is shown in figure 3 with the increasing decay rate of the current as the field is increased. More importantly, the effect is seen in figure 4. The field dependence of the peak photocurrent below a critical current is superlinear in field varying approximately as $I_P \propto E^{1.8}$.

Above this critical current the dependence is much weaker, varying approximately linearly with field. This critical current is the same as that observed for the switch from linear to square-root dependence of I_P on N_{PH}, being 1 mA. The change in field dependence is then a consequence of the change from linear to square-root dependence of I_P on generation rate. At fields below the change over the current varies with field to the power 1.8. This is because $\varphi(E)$, the probability of avoiding geminate recombination has this variation. The generation rate, G, is given by

$$G = N_{PH}\eta\varphi(E) \tag{6}$$

where η is the efficiency of carrier pair photogeneration.

In the recombination limit then

$$I_P \propto \sqrt{G} = \sqrt{(N_{PH}\eta\varphi(E))}. \tag{7}$$

One then expects $I_P \propto E^{0.9}$ in the recombination regime if the field dependence away from this regime is only due to $\varphi(E)$ as proposed here. This is essentially what is observed. If the carrier velocity was linearly dependent on field, then from the overall field dependence of I_P ($\propto E^{1.8}$) away from the recombination regime, a variation, $\varphi(E) \propto E^{0.8}$, would be deduced. Thus, in this regime, one would predict $I_P \propto v\sqrt{\varphi} \propto E^{1.4}$, contrary to these measurements. These results are then a completely new way of demonstrating that the field dependence of the generation rate is the sole determining factor in the field dependence of I_P. This then demonstrates that the drift velocity is independent of field.

5. Conclusions

The work described here has demonstrated that:

(i) Previous workers (Moses and Heeger, 1989), observing an increase in decay rate as field increased were erroneous in their attribution of this to a linear increase in drift velocity. The increase of decay rate is due only to an increase in bimolecular decay time, $(\beta n)^{-1}$. This is made evident by the close correlation of photocurrent decay as light or electric field is varied.

(ii) Carriers on chains separated by up to 60 chains may Coulombically interact, and in the case of oppositely charged carrier pairs undergo pseudo recombination.

(iii) The carrier generation rate is the only mechanism contributing to the field dependence of the peak photocurrent observed here and the photocurrent varies as the square root of this generation rate when it rises above a critical value. Furthermore, this critical change over is exactly mirrored in the intensity dependence of the photocurrent.

Finally, the results presented here have re-enforced in a novel way many previous experiments that have demonstrated that the drift velocity is independent of electric field.

Acknowledgments

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References

Blossey F D 1974 *Phys. Rev.* B **9** 5183
Donovan K J, Freeman P D and Wilson E G 1985 *Polydiacetylenes* ed D Bloor and R Chance (Dordrecht: Martinus Nijhoff) p 165
Donovan K J and Wilson E G 1981a *Phil. Mag.* B **44** 9
—— 1981b *Phil. Mag.* B **44** 31
—— 1989 *Synth. Met.* **28** D563
—— 1990 *J. Phys.: Condens. Matter* **2** 1659
Gogolin A A 1988 *Phys. Rep.* **157** 348
Haberkorn R and Michelle-Beyerle M E 1973 *Chem. Phys. Lett.* **23** 128
Moses D and Heeger A J 1989 *J. Phys.: Condens. Matter* **1** 7359
Seiferfeld U, Ries B and Bassler H 1983 *J. Phys. C: Solid State Phys.* **16** 5189
Siddiqui A S and Wilson E G 1979 *J. Phys. C: Solid State Phys.* **12** 4237
Wilson E G 1980 *J. Phys. C: Solid State Phys.* **13** 2995
—— 1983 *J. Phys. C: Solid State Phys.* **16** 6739
—— 1989 *Synth. Met.* **28** D551