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ELECTRON-ELECTRON INTERACTIONS AND COULOMB GLASS CREATION IN ELECTRONIC ONE DIMENSIONAL SYSTEMS

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ABSTRACT Experimental evidence is presented that demonstrates how a light pulse incident upon a 1D semiconductor, PDATS, in zero field, seeds that semiconductor with charge held in a stable state, unrecombined, for times on the order of milliseconds. Application of an electric field at later time releases some of this seed charge which is measured whilst the remainder recombines. Two models for this effect are put forward and discussed and an idea for a molecular logic unit, the transactor, is introduced.

INTRODUCTION

Diacetylenes with the appropriate sidegroups may be polymerised in the solid state to give macroscopic, highly perfect single crystals of polydiacetylene. Much work has gone in to understanding the electronic transport properties of one such polydiacetylene, the toluene sulphonate derivative PDATS. The covalently bonded carbon backbone of the polymer chain forms a one dimensional, 1D, semiconducting system with weak Van der Waals bonding to its nearest neighbour at 7A distance and low interchain electron transfer as a result.

An almost universal conclusion from this work is that photocarrier generation efficiency is linear in electric field[1,2,3]. This, it has been argued, is a property of 1D semiconductors where the probability of an electron escaping its twin hole and subsequently contributing to a photocurrent is linear in field becoming zero in zero field, a consequence of the random walk in 1D. More recently, studies have demonstrated that after a 25ps light pulse has created mobile charge uniformly within a crystal of PDATS, an electron will drift in an electric field along the chain it was created on until finding a hole created in the same light pulse. Provided that the hole is on a chain within 60 chains of the electron, the electron-hole pair will

immobilise each other on the timescale of ten nanoseconds[4], the process having all the characteristics of bimolecular recombination, such as a peak photocurrent value that varies as the square root of the number of photons, N, in the exciting light pulse, and a decay rate of the photocurrent that increases with N.

Such pseudo-bimolecular recombination differs from the normal situation in eg silicon, in that the carrier pair immobilise one another but do not recombine, as interchain transfer is considerably difficult. The pair then remain available to retake part in the photoconduction process at a later time should a thermal fluctuation or an increased electric field contrive to separate them once more.

In the present work a further remarkable behaviour is described and its existence ascribed to the one dimensionality of the PDA's. It is observed, that if the crystal is illuminated by a laser pulse with no field applied until a time τ_d later, there is nevertheless substantially the same quantity of photocharge, $Q_{Ph}(\tau_d)$, collected as would have been the case if the same field had been applied continuously. This remains true for τ_d up to and beyond milliseconds and implies that some initial charge is generated in zero field, a fraction of which may be seperated at a later time by application of a field. This initial charge is long lived and therefore in some way true recombination is inhibited. This remarkable observation throws up two questions both linked:

1) Why does any charge at all avoid geminate recombination in these ideal 1D systems, and how much survives such an immediate fate?

2) Is there a stable configuration of the electrons and holes enabling them to avoid recombination of any kind for such a long time?

EXPERIMENT

Crystals of PDATS were furnished with surface electrodes, separated by a gap of width d = 250μm, in such a way as to apply a field in the polymer chain direction when a voltage was applied across the gap.

In these experiments one side of the gap is connected to an electrometer measuring charge arriving at the electrode. The other side is held at ground potential until a time τ_d after the gap has been

illuminated by a laser pulse from an N_2 laser (photon energy 3.68eV, pulse duration 6ns). After the time τ_d the potential is raised rapidly to apply a field across the gap. This results in the flow of a dark current, I_D, plus the sweepout of any available photocharge remaining from the laser pulse after the time τ_d, $Q_{Ph}(\tau_d)$. The charge collected as a function of time is monitored on a chart recorder. This charge, Q(t), is then made up of three components

$$Q(t) = \int I_D dt + Q_{Disp} + Q_{Ph}(\tau_d) \qquad (1)$$

Here Q_{Disp} is a displacement charge resulting from the change in voltage. By measuring Q(t) with no laser pulse present and subtracting this from the value when a laser pulse is incident on the gap, $Q_{Ph}(\tau_d)$ is found.

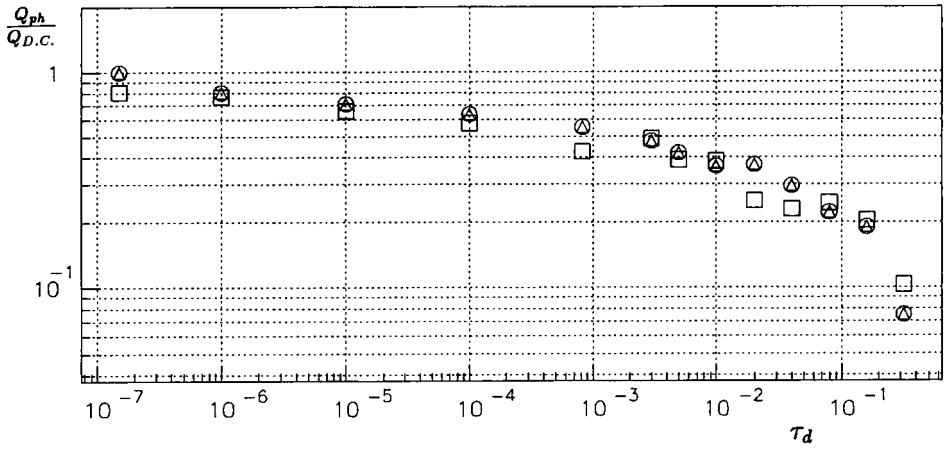

FIGURE 1 A plot of $Log(Q_{Ph}/Q_{DC})$ vs $Log(\tau_d)$. The field is varied with: circles 280 kVm^{-1}, squares 120 kVm^{-1} and triangles 40 kVm^{-1}.

RESULTS

The quantity of charge extracted upon application of a field, E, at a time τ_d after a laser pulse has excited the PDATS crystal is shown in figure 1 on a log-log plot. The charge is normalised to the amount of charge extracted when E is on all the time, Q_{DC}. The data of figure 1 is taken at three different fields and demonstrates a very slow roll

off of the charge collected over many decades in time, the form of which is independent of field. By inference the field dependence of $Q_{Ph}(\tau_d)$ is independent of τ_d and is identical to the dependence observed when a field is present continuously, ie the DC case.

DISCUSSION

Figure 1 demonstrates that charge created with a fast laser pulse in zero field may avoid immediate geminate recombination and be held for durations of up to milliseconds without substantial recombination of any kind. Two mechanisms for achieving this effect are indicated schematically in figures 2a and 2b and explored in what follows.

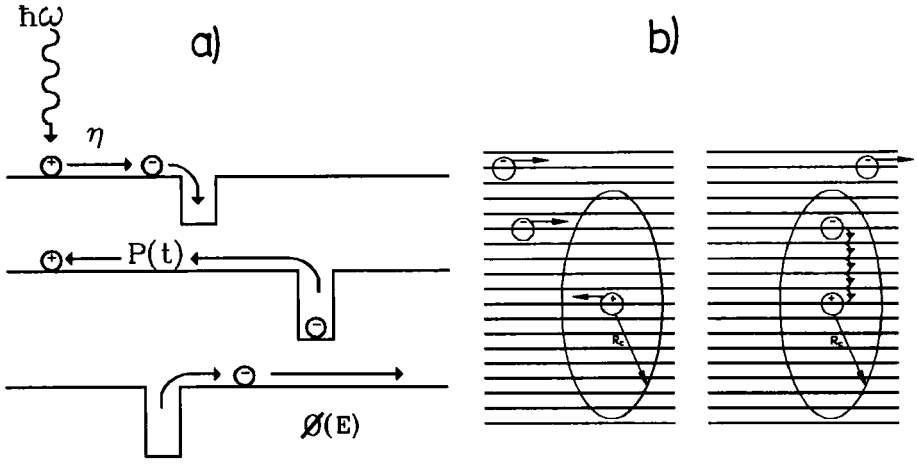

FIGURE 2 a) Model 1 discussed in the text. b) Model 2 discussed in the text.

Model 1: Charge storage in traps.

In this model (figure 2a) it is envisaged that light creates carrier pairs with efficiency η, and that a fraction of the pairs, f, avoid geminate recombination in zero field by rapid on chain diffusion to traps. Over time trap release events occur and there is a probability, $p(t)$, that after a time t, recombination has occurred with the twin carrier. This probability is proportional to the amount of time spent as a free carrier, τ_f, during the time t. Upon application of an

electric field after a time τ_d a field dependent fraction, $\phi(E)$, of those carriers still unrecombined, will escape completely to be collected as the measured charge, $Q_{Ph}(\tau_d)$, of this experiment.

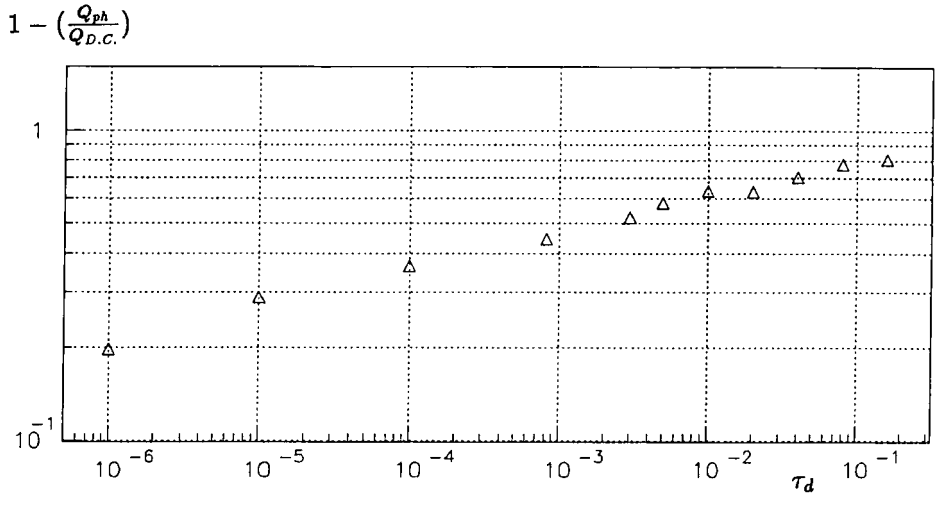

FIGURE 3 A plot of Log $(1-Q_{Ph}/Q_{DC})$ vs Log(τ_d) with the data taken from figure 1 for E = 40kVm^{-1}. The slope is β=0.12.

To reproduce the curves of figure 2 a distribution of trap depths and trap release rates must be assumed. Movaghar used such a distribution to explain the long time decay of pulsed photocurrents in PDATS[5]. In that model the photocurrent decay is attributed to the decreasing average carrier velocity, v, with time as carriers drift in 1D through a trap distribution. Experiment and model showed that v is proportional to $t^{-\alpha}$ with α = 0.85. From this it follows that

$$p(t) \propto \tau_f \propto t^{1-\alpha} \tag{2}$$

The number of carriers recombined after the time τ_d is given by

$$N_{Rec}(\tau_d) \propto (1 - Q_{Ph}/Q_{DC}) \propto p(\tau_d) \propto \tau_d^{1-\alpha} \tag{3}$$

Figure 3 shows a plot of Log$(1-Q_{Ph}/Q_{DC})$ vs Log(τ_d) taken from the data of figure 1. Figure 3 recovers the dependence of equation 3 with α

= 0.88 in close agreement with the α from the photocurrent decay.

The parameter α in this model is related to a trap depth distribution $\rho(\epsilon)$ of the form $\exp(-\epsilon/kT_M)$ with $\alpha = (1 - T/T_M)$. This model requires a distribution of trap depths, $\rho(\epsilon) = \exp(-\epsilon/208meV)$.

Recalling the highly crystalline nature of the PDATS samples it may seem improbable that a trap distribution that has found fame in describing amorphous silicon is equally applicable here. Indeed it is hard to see how such a broad distribution may arise.

Model 2: Interchain excitons and a coulomb glass.

Another and more exotic possibility is that photoexcited electrons and holes initially separate by diffusion as before. However, now what prevents geminate recombination is the formation of interchain excitons. That is, the electron on one chain comes under the coulombic influence of a hole on an adjacent chain (figure 2b). Provided this electron-hole pair lie within a coulomb radius of each other their mutual attraction may be greater than the attraction of the electron/hole for its twin on the same chain. Because the pair forming the interchain exciton are on different chains any immediate recombination is precluded.

Eventual recombination may proceed in two ways. The carriers forming the exciton may finally recombine as interchain tunnelling brings them together, or thermal fluctuation may lead to a pair breaking up and the electron/hole forming new more tightly bound excitons by diffusive on chain motion and finding new partners. Application of a field may diminish the effective coulomb binding energy of a pair and lead to their seperation and collection as the charge Q_{Ph}. At a given field only excitons of radius greater than some critical radius r_{crit} would be seperated by that field. With increasing time the number of excitons with a radius satisfying that criteria would diminish and this is the decay in Q_{Ph} as τ_d is increased. At any given time the number available for separation would be greater for larger fields causing the observed E field dependence. Those excitons with a radius less than the critical radius will eventually recombine. In addition, the probability of escape of a carrier from its coulomb twin on an adjacent chain would be expected to have the 1D Onsager dependence on field. In this explanation of events, the time taken in

zero field for the charge to recombine will depend on the shorter of the time taken to cross chains and recombine or the time taken to find a recombination partner once released by thermal fluctuation. If it is the latter process then it would be possible to map model 1, and its explanation of the form of figure 2, onto model 2.

Such an interchain exciton model allows other possibilities than the simple electron-hole structure described above. For example, whole collections of electrons and holes may build up into a collective entity interacting via the coulomb interaction. The short term constraints are that the carriers remain on the chains they are created on and that the ensemble of carriers adjusts itself such that the coulomb energy is minimised. This is analogous to the coulomb glass[6], where a collection of positive and negative charges are given a set of sites to distribute themselves over and take up configurations which correspond to local minima in the total coulomb energy.

The coulomb glass/interchain exciton is thus a further explanation of the observations presented here. It is a natural mechanism for providing what would appear to be a broad spectrum of trap depths from the deeply bound excitons on adjacent chains to those excitons with a radius equal to the coulomb radius, $r_{kT} = e^2/4\pi\varepsilon\varepsilon_0 kT$, bound with energy kT. Such phenomena should be expected to occur in anisotropic systems. The existence of such a coulomb glass at high carrier density or even of a stable interchain exciton raises other interesting possibilities.

THE TRANSACTOR: A POTENTIAL MOLECULAR ELECTRONIC SWITCH.

One example of the use to which long range coulomb effects may be used in a controlled manner is the "Transactor", due to Wilson, figure 4. PDA's may be deposited as LB films. Consider two PDA layers deposited in a controlled manner such as to leave the chain directions, c and c′ in the two layers mutually orthogonal. With surface electrodes deposited such as to apply an electric field at 45^{o} to both sets of chains and the ends of the chains illuminated by a spatially localised pulse creating electrons and holes, the electrons will move towards the region of overlap of the two layers in one layer whilst the holes move to this region in the other as shown schematically in figure 4.

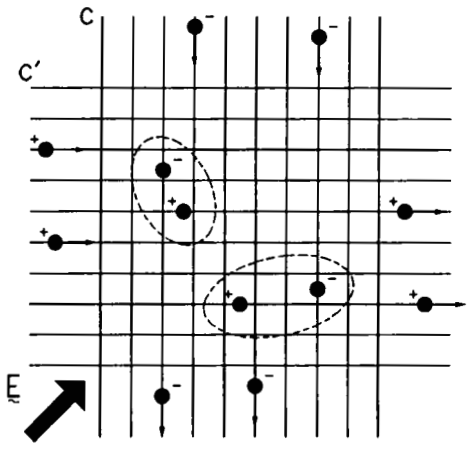

Figure 4. The transactor described in the text. Two layers of PDA LB film with orthogonal chain directions. By coulomb binding holes and electrons in adjacent layers a logic gate is formed.

In these and other experiments we have seen how easily an electron may immobilise a hole on an adjacent chain. Thus if electrons on one layer arrive contemporaneously with holes in the other, current will cease to flow in both layers. In this way control of pulses of holes in one layer by electrons in the other is achieved at a molecular level. This is very much work in progress and the many ramifications of the coulomb glass model are still to be explored.

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