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OBSERVATION OF CHARGE MOTION ALONG MOLECULAR WIRES LAID DOWN AS LANGMUIR-BLODGETT MULTILAYERS

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ABSTRACT Fast photocurrents have been observed in Langmuir-Blodgett multilayers of polymerised 10,12 penta cosa diynoic acid (PDA 12-8). They are linear in electric field and vary sublinearly with light intensity.

Keywords: Polydiacetylenes, 1-dimensional conduction, Langmuir-Blodgett multilayers

INTRODUCTION

Experiments have shown that the conjugated backbone of polydiacetylenes may act to transport free charge carriers over macroscopic distances under the influence of an electric field in the chain direction[1]. A series of experiments on the macroscopic single crystal polydiacetylene Toluene Sulphonate have demonstrated that the transport is unique. It was demonstrated that the drift velocity is saturated at about the velocity of sound independent of applied field even at the lowest fields experimentally usable[1]. This unique motion has since been explained theoretically as being due the fact that a free charge carrier forms a Solitary Wave Acoustic Polaron, SWAP[2]. These measurements have been extended to chain extended polydiacetylenes in solution[3]. The motion of the SWAP is expected to be of use in Molecular Electronics as the drift velocity and transit times of carriers would be impervious to local variations in the electric field which would be expected to occur. In this work we extend the observation of carrier motion to Langmuir Blodgett films of polydiacetylenes as these structures would seem to be obvious candidates in developing an actual Molecular Electronic device. Some initial results of this investigation using the PDA 12-8[4] are presented.

EXPERIMENTAL

Multilayers of 12-8 diacetylene were formed on quartz substrates by the

Langmuir-Blodgett (LB) technique[4] using an MGW-Lauda film balance. The substrates were pre-cleaned by sonication in alcoholic sodium hydroxide solution and made hydrophobic by immersion in dimethyldichlorosilane solution. The subphase was adjusted to a pH of 6.25 and cadmium chloride was added to a concentration of 0.1mMol. The layers were deposited at a rate of 150μm/s.

The LB layers were UV polymerized to the blue phase prior to vacuum deposition of the of the silver electrodes. Wire contacts were then bonded to the electrodes using a silver-loaded paste. Finally, the structure was spray-coated with a clear pcb lacquer (Electrolube Ltd., ref: cpl 200 H) to prevent photoemmision from the electrodes. The PDA layers changed from the blue phase to the red phase[5] as a consequence. A schematic of the structure is shown in figure 1a. Samples of 20, 30 and 40 LB layers were produced.

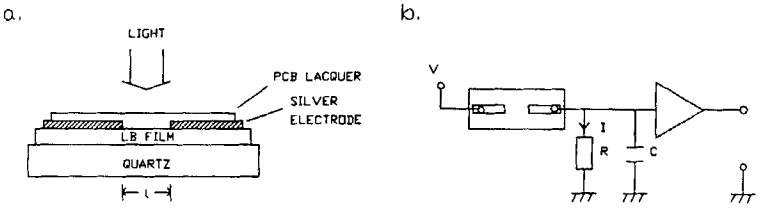

FIGURE 1 Schematic diagrams of the samples (a) and the measuring circuit (b).

Phototransients were measured by biasing the sample and irradiating with light pulses of 25ps duration from a frequency doubled, passively mode-locked Nd YAG laser (JK Lasers). The photon energy is 2.33eV. The transients were amplified and displayed on a storage oscilloscope as shown in figure 1b.

RESULTS AND DISCUSSION

A typical phototransient signal is shown in figure 2. The transient decay time is faster than the electronic response of the measuring circuit. It is clear from this that the majority of the carriers do not, on the time scale of the experiment, reach the electrodes but instead travel a

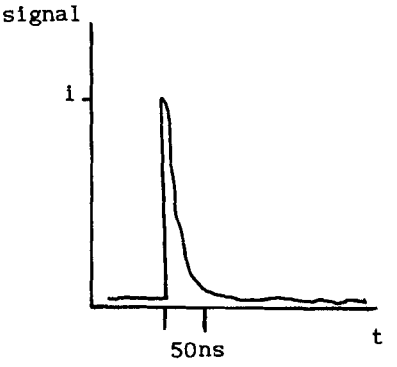

FIGURE 2 A typical phototransient signal.

smaller distance, s. This is expected from the micron sized domain structure of the LB layers where carriers are stopped at the grain boundaries (or, indeed, at smaller distances if sufficiently deep traps are present within domains).

Figure 3 shows the dependence of the peak signal, i, with

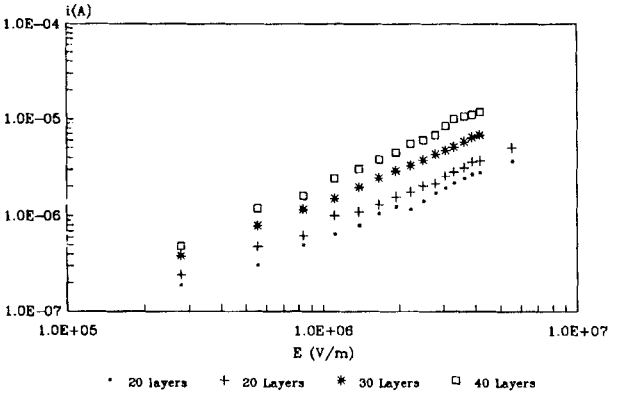

FIGURE 3 Variation of peak signal with electric field.

applied electric field, E. A general scaling with number of layers is seen. The two data sets with 20 PDA layers shows the typical sample to sample variation. The peak signal itself is linear in electric field. Suppose that carriers have travelled a distance s before trapping/recombining. Then

$$Q = ne\eta\Phi(E)\ s/l \tag{1}$$

where Q is the charge induced at the electrodes, n is the number of photons absorbed, e is the electronic charge, η is the quantum efficiency of carrier pair generation, $\phi(E)$ is the probablity of avoiding geminate recombination and l is the electrode gap. Further,

$$i = Q / (RC) \tag{2}$$

where C is the stray capacitance and R is the measuring resistance. In a 1-D system s is field independent. 1-D Onsager theory[6,7] predicts a linear to superlinear dependence of ϕ on E.

From equation (1) we have that for a given light intensity and applied field, Q will be independent of the gap spacing, l, provided that s is constant and less then l. Figure 4 shows i against E for two

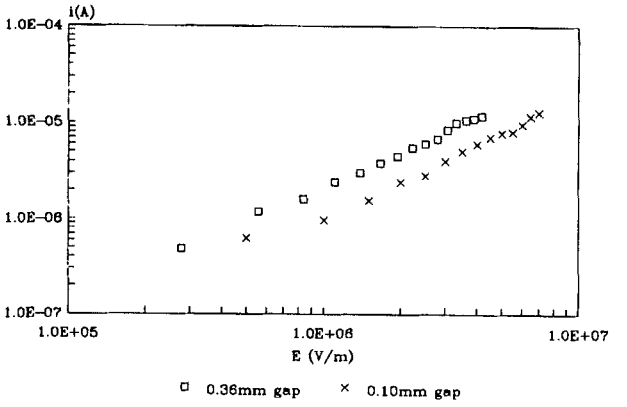

FIGURE 4 Variation of peak signal with electric field for two different gap sizes.

gap spacings with l = 0.36mm and l = 0.1mm. Although there is some variation with l, it is at this stage not unreasonable to suggest that this may be due to sample to sample variation of s.

The measured signal, i, has a power law dependence on light intensity, $i = I^m$, where $m \cong 2/3$, figure 5. Even over the limited

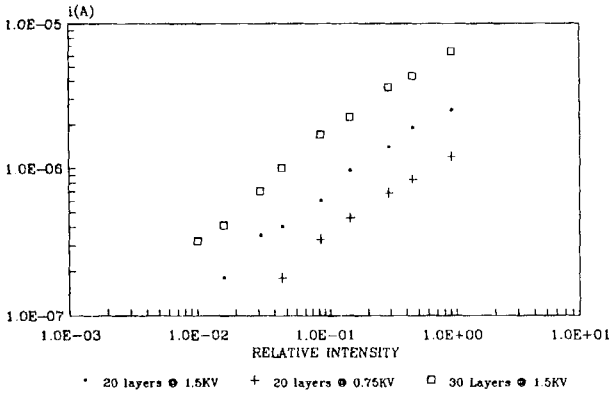

FIGURE 5 Variation in peak signal with light intensity.

intensity range, it appears that m is neither 1, characteristic of unimolecular recombination, nor 1/2, characteristic of bimolecular recombination, but that $1/2 < m < 1$. We consider this is due to both loss processes occurring in different regions of the sample.

The electric field is highly non uniform[8]. For a generation linear in field, as in the 1D Onsager theory, then generation is also highly non uniform. Thus it may be possible for the region of high field and carrier density adjacent to the electrodes to be subject to bimolecular recombination, yet the sample centre be to be controlled by unimolecular loss processes; the sample as a whole can then be controlled by a composite of both loss mechanisms. This view is being developed and tested.

Frankevich et al[9,10] have seen $2/3 < m < 1$ in bulk PDA crystals with surface electrodes. They offer a model, involving recombination, which would make the existence of the phenomenon $1/2 < m < 1$ a material

property. However Willock[11] has shown that bulk crystals with bulk electrodes, having m = 1 and m = 1/2 dependence, go over to displaying m ≅ 0.72 behavior on applying surface electrodes to the same samples. This is evidence that electrode geometry is important.

These questions of generation and recombination are being pursued and will be reported on in the future.

CONCLUSIONS

We have demonstrated that photcurrents can be generated in LB PDA multilayers. Dependences of induced charge as a function of applied field and light intensities have been reported. The dependence on light intensity is complicated and requires further study. The linear field dependence is due to field dependent generation processes, and therefore the distance to trap/recombine must be field independent as expected for a 1-D material. It is hoped to improve the temporal resolution of these experiments, and using smaller gap widths, observe motion within single domains.

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