Quenching of the magnetic field effect on the photocurrent and photocurrent detected magnetic resonance in conjugated polymer - fullerene diodes

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ABSTRACT

We have studied the effect of a magnetic field on the photocurrent of MDMO-PPV (poly(2-methoxy,5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene) and MDMO-PPV/fullerene diodes (plastic solar cells) and performed photocurrent detected magnetic resonance (PCDMR) experiments on these devices consisting of an active layer sandwiched between a low and a high workfunction metal electrode. Results clearly show that the magnetic field effect (MFE) on the photocuttent as well as PCDMR signals are quenched in conjugated polymer/fullerene composite devices in contrast to large signals observed in the pristine conjugated polymer devices. Photoinduced electron transfer from conjugated polymers onto fullerene is proposed to be responsible for this quenching.

INTRODUCTION

Photo-induced electron transfer in solid-state composites of conjugated polymers and fullerenes has attracted considerable scientific and technological attention [1]. The possibility of utilising this effect for photo-voltaic energy conversion is especially interesting [1]. The photo-induced forward electron transfer occurs within 100 fs and the charge-separated state is very long lived [1]. By doping the conjugated polymer matrix with a few wt % of fullerene a strong quenching of the photoluminescence and an increase of the photo-conductivity of nearly two orders of magnitude has been observed [1].

Light-induced electron-spin-resonance (LESR) studies have been reported revealing the appearance of two LESR signals [1,2]. These signals are attributed to the radical anion of the fullerene molecule and the positive polaron on the conjugated chain. For composites of MDMO-PPV/PCBM (1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61} g-values of g=1.9995 ($PCBM^-$) and g=2.0025 have been reported [2]. While ordinary ESR is best suited for large volume samples it is often not sensitive enough for applications in thin layered samples and especially in active devices. One has to use other magnetic resonance techniques e.g. optically detected magnetic resonance (ODMR) or electrically detected magnetic resonance (EDMR). Usually these experiments are based on the fact that the recombination of the photo-generated charge carriers depends on their relative spin orientation. Observing a process e.g. delayed luminescence or photo-conductivity ESR transitions can change the spin orientations and therefore the yield of the observed property. Especially ODMR and EDMR are well established and powerful spectroscopic techniques to study the recombination properties in inorganic semiconductors and as recently shown also in organic systems like conjugated polymers

[3]. Magnetic field effect (MFE) and photo-current detected magnetic resonance studies have already been reported for photocells based on conjugated polymers alone [4,5]. These experiments suggest that so-called polaron pairs are formed as an intermediate state after photo-excitation [4,5].
For different PPV's a positive MFE on the photo-current has been reported [4] and a decrease of the photo-current under microwave resonance conditions [5].
We are especially interested in the physical processes occurring in a photo-voltaic device based on a blend of MDMO-PPV/PCBM. For these photocells energy conversion efficiencies of 0.7 % (under AM1.5 conditions) have been reported [6], they can be prepared on flexible substrates and are very promising for low cost applications.

EXPERIMENTAL

The arrangement of the thin film devices is shown in Fig. 1. The substrates were cleaned and etched using standard procedures described elsewhere [7]. After depositing a PEDOT (poly(ethylenedioxythiophene) and a photo-active film by spincast or doctor balding technique, aluminium is evaporated as second electrode. All films were prepared from solutions holding the same concentration of MDMO-PPV (0.28 %(wt)) and having a thickness of ~100nm. For the investigation of the magnetic field effect on the photo-current sealed devices with an active area of $4cm^2$ were placed between a pair of Helmholtz coils. The devices were homogeneously illuminated by an Ar+-Laser (488nm) and the photo-current was measured by a Keithley 2400 SMU. The photo-current detected magnetic resonance experiments were carried out using devices with an active area of 4 mm^2. The samples were contacted with thin copper wires and sealed in a NMR-tube in Ar-atmosphere and placed in a rectangular TE_{102} cavity with two windows for optical access inside the magnet of a commercial X-band ESR-Spectrometer (Bruker EMX). The microwave power (up to 200.7mW) was modulated with a p-i-n modulator. The gun diode frequency was locked to an additional cylinder cavity. Samples were excited either by an Ar+-Laser or a xenon lamp spectrally dispersed by a single grid monochromator. A lock-in amplifier was used to detect the synchronous changes of the photo-current on the square-wave modulated microwave power while gradually sweeping the magnetic field. Due to the rather slow response of the electrical signal on the modulation of the microwave

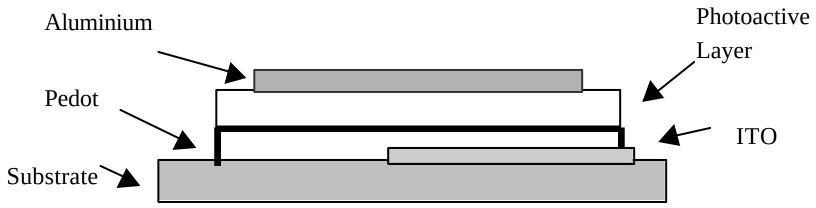

***Figure 1**. Device structure*

irradiation all the PCDMR experiments were carried out at low (microwave power) modulation frequencies (<200 Hz). All experiments presented here were performed at ambient temperatures.

EXPERIMENTAL RESULTS

Figure 2 shows the comparison of the magnetic field effect on the short circuit photo-current in a MDMO-PPV and a MDMO-PPV/PCBM device measured at room-temperature. Under these conditions a MFE could only be observed for a diode based on pristine conjugated polymer alone. In the plastic solar cell no change of the photo-current was found. The observed characteristics did not depend on the direction of the external magnetic field. A MFE on the photo-current of similar magnitude has already been observed by Frankevich et al. in PPV and PPPV [4].

Figure 3 shows the PCDMR-spectrum of a MDMO-PPV diode detected via short circuit current at 298K. The signal consists of one line with g=2.0029, $\Delta B_{1/2}$=7G. No triplet spectra have been found neither at half-field nor around the central resonance line. Similar results have been reported by Dyakonov et al. for PPV-diodes synthesised via the precursor route [5]. However we observe a two orders of magnitude smaller decrease of I_{SC} at room temperature. In contrast to the conjugated polymer, the MDMO-PPV/PCBM device shows no changes of I_{SC} when the magnetic field is swept under microwave irradiation. To investigate the influence of the amount of fullerene present in the device on the PCDMR signal cells with different fullerene concentrations have been prepared.

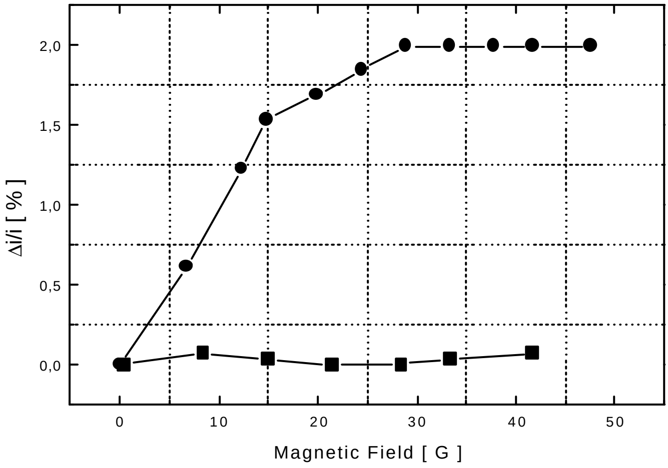

Figure 2. *Magnetic field effect on the short circuit photo-current. Squares MDMO-PPV/PCBM diode, circles MDMO-PPV device*

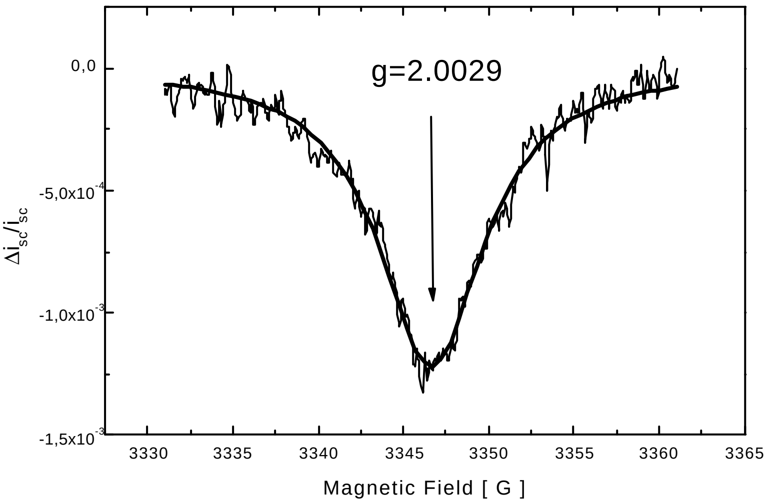

Figure 3. *PCDMR-Spectrum of a MDMO-PPV Diode. Light illumination 5 mW/cm^2 488nm, 200.7mW microwave power*

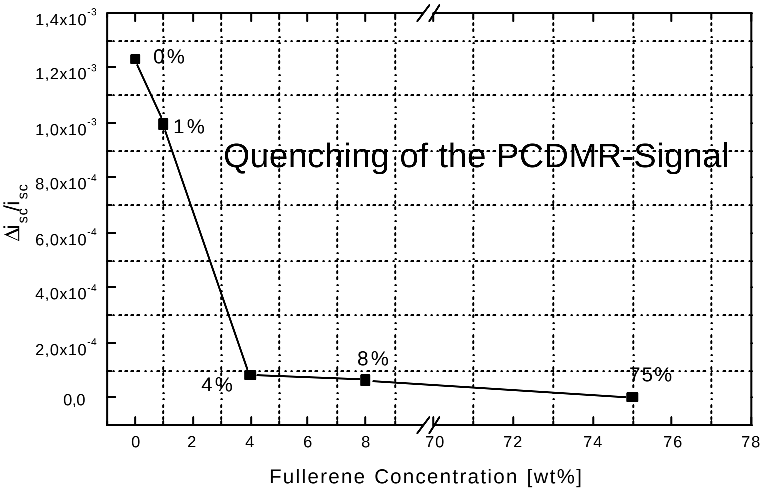

Figure 4. *Amplitude of the PCDMR-signal for different fullerene concentrations in MDMO-PPV*

Figure 4 shows the amplitude of the PCDMR-signal ($\Delta I_{SC}/I_{SC}$) as a function of the fullerene concentration. By adding a few wt% of PCBM the signal decreases by one order of magnitude and can not be observed at high fullerene concentrations.

DISCUSSION

The experimental results shown above for the devices based on pure conjugated polymers can be discussed in the frame of polaron pairs [8]. An absorbed photon creates a singlet excited state on the polymer chain. A fraction of these excited states dissociates and spin-correlated radical pairs (polaron pairs) are formed. These pairs are initially formed in a state having mainly singlet character. They can dissociate and contribute to the photo-current or recombine. The recombination process is spin dependent. An external magnetic field can change the population rate of the spin states and can also change the intersystem crossing probabilities. If the different spin states have different probabilities for recombination and dissociation the yield of e.g. the free charge carrier generation can be changed by an external magnetic field. An additionally applied resonant microwave field redistributes the spins further and therefore a change of the reaction yield is also observable under resonance conditions.

All the negative results for the devices containing significant amounts of fullerenes are not understood up to now. Here the primary excitation results in a charge transfer from the conjugated polymer to the fullerene. Either the spin-correlation between the created charge carriers is destroyed immediately or no pairs are formed at all. Further investigations of the influence of an electric field on the MFE and PCDMR spectrum might help the get some better understanding of the processes occurring in the plastic solar cell.

ACKNOWLEDGEMENTS

We would like to thank Prof. E. Frankevich for valuable discussions and Dr. Gerald Zerza for experimental help. M.C.S acknowledges financial support by the Magistrat Linz and the Hochschulfond.

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