Diffusion photovoltage in poly(p-phenylenevinylene)

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Photovoltage phenomena in poly(*p*-phenylenevinylene) (PPV) are investigated under pulsed laser illumination. The photovoltage transients are strongly retarded in time depending on sample thickness, laser intensity, and bias illumination. It is shown that the photovoltage in PPV originates from separation of excess electrons and holes due to their concentration gradient and different diffusion coefficients (diffusion photovoltage). The diffusion coefficient of excess holes is found to be on the order of 1×10^{-6} cm^2/s and it increases with increasing excitation intensity and intensity of bias illumination. The diffusion coefficient of excess electrons is about 1–2 orders of magnitude smaller than for excess holes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1355721]

I. INTRODUCTION

Organic molecular semiconductors as poly(*p*-phenylenevinylene) (PPV) are intensively investigated for optical applications due to their high luminescence efficiency.[1–3] The transport of charge carriers is important for the performance of light-emitting devices. For PPV, the drift mobility of excess holes which was determined from the time-of-flight (TOF) measurements[4] is on the order of 10^{-6}–10^{-5} cm^2/V s. The drift mobility of excess electrons is much smaller as shown in transient electroluminescence measurements.[5] The TOF method requires an application of bias electrical field without significant carriers injection. This complicates the TOF investigation and its interpretation under injection conditions. In this work we show that the diffusion coefficients of excess holes (D_p) and electrons (D_n) in PPV can be investigated by photovoltage measurements even under injection condition as constant bias illumination.

The spatial separation of excess charge carriers causes photovoltage (PV) which depends on carrier transport. The photovoltage technique is a powerful tool for the investigation of the carrier lifetime,[6] surface potential,[7] or surface state distribution,[8–10] states in the forbidden[11] gap in crystalline semiconductors. The Maxwell relaxation time (τ_M) in crystalline semiconductors at room temperature lies usually in nanosecond-range. The well known processes of PV formation by band flattening and so-called Dember PV due to different drift mobilities of excess electrons and holes are well described for the times larger than τ_M. The value of τ_M is huge in dielectrics, such as PPV. This should modify the transient behavior of PV. We observed strongly retarded PV transients for PPV. It will be shown, that diffusion of excess electrons and holes with different diffusion coefficients is responsible for the formation of PV in PPV.

II. EXPERIMENT

Layered PPV films were prepared on indium–tin–oxide (ITO) coated glass substrates by thermal conversion of a soluble precursor as described in Ref. 4. Samples of three thicknesses were fabricated: 90 nm (thin), 290 nm (medium), and 780 nm (thick). The PV measurements were carried out in a plate capacitor scheme. It consists of the PPV layer on the glass substrate with ITO, a 10 μm thick mica spacer and a semitransparent Cr electrode evaporated on a quartz homogenizer. Illumination was performed through the quartz with the Cr electrode (front side illumination) or through the glass substrate with the ITO back contact (back side illumination). PV transients were investigated on the time scale between 1 ns and 0.01 s. Charging of the capacitor via the high resistance limits the measurements to times less than RC=0.01 s (*R*-load resistance 1GΩ, *C*-capacitance of the measurement structure).

A N$_2$ laser (wavelength $\lambda = 337$ nm, pulse duration 4 ns, maximal intensity $I_0 = 300$ μJ/cm^2) was used for the excitation of PV transients. The respective absorption length is about 10^{-5} cm^{-1} for PPV. Therefore, the excess carriers were generated homogeneously in the thin sample while a strong gradient of excess carriers appeared in the thick sample. A 1000 W Xe lamp with a quartz-prism monochromator is used for constant bias illumination.

III. RESULTS AND DISCUSSION

Figure 1 shows typical PV transients of the thick sample for front (b) and back (a) side illumination. The transients are strongly retarded in time in comparison to the duration of the laser pulse. This retardation differs from PV transients in conventional semiconductor,[12,13] where PV amplitude reaches a maximum within 100 ns after laser pulse action. The positive (negative) sign of PV under back (front) side illumination corresponds to the faster propagation of positive charge carriers in PPV. This means that $D_p > D_n$. Variations
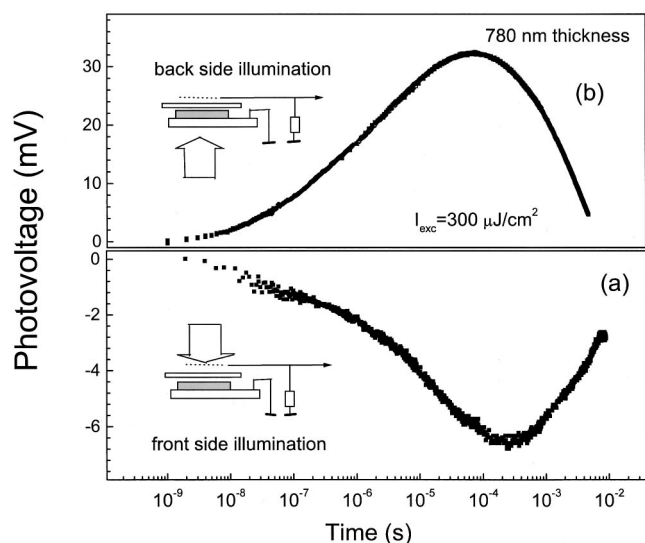
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FIG. 1. Photovoltage transients of the thick sample (780 nm thickness) at a front (b) and back (a) side illumination.

FIG. 3. Simulated transients for different hole diffusion coefficients and different ratios between hole and electron diffusion coefficients.

of the absolute value of amplitude and time position of minimum (maximum) is due to different illumination intensities (absorption by the Cr electrode).

Figure 2 shows PV transients of the thin sample for front and back side illumination. These transients are also strongly retarded in time but of the same sign. We suppose that the concentration gradient is a driving force for the separation of excess electrons and holes also for the thin sample. The concentration gradient appears due to the injection of holes into the ITO (ITO/PPV is the ohmic contact for holes). The sign of this process is independent of front or back side illumination. The time of maximum of PV transients (t_{max}) is about one order shorter for the thin sample than for the thick one. For the sample with medium thickness, t_{max} is between t_{max} of the thin and thick samples. As remark, the PV transients of the sample with medium thickness depend very sensitively on the illumination condition due to the superposition of diffusion and injection processes.

However, the dependence of t_{max} does not allow us to determine directly the diffusion coefficient of excess charge carriers, since the change of τ_M with the change of charge carriers concentration should be taken into account. There-
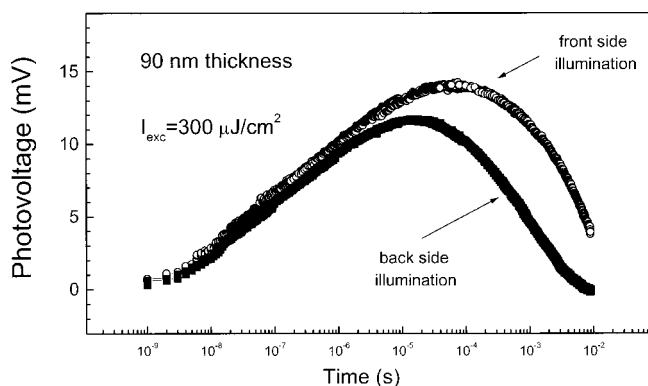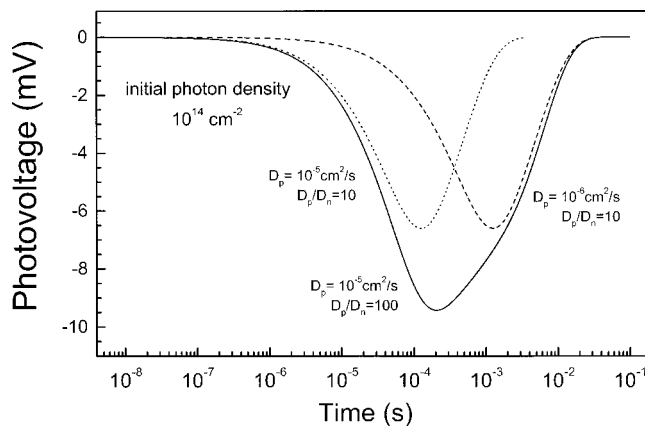
fore, computer simulations of PV transients which consider diffusion and drift are necessary for the determination of D_n and D_p.

We solved numerically the one dimensional Poisson and continuity equations for electrons and holes. Diffusion and drift were taken into account. The dielectric constant of PPV was taken as 4. Integration of the electrical field over the thickness of the sample gives the value of PV. Figure 3 shows a typical example for the influence of D_p and D_n on different calculated PV transients. The value of t_{max} is determined by the faster component of the diffusive carriers, i.e., D_p. The ''width'' of the transient (log–log scale) depends sensitively on the ratio D_p/D_n. The shapes and amplitudes of the calculated PV transients agree with the measured PV transients (Figs. 1 and 2).

Figure 4(a) shows PV transients for the thick sample (front side illumination) at different excitation levels. The increase of the illumination intensity causes an increase of the PV amplitude and a decrease of t_{max}. The numerical simulation of PV transients at different excitation levels are given in Fig. 4(b). The simulated PV transients show the same tendency as the measured PV transients and the calculated PV amplitudes and values of t_{max} are satisfactory. This

FIG. 2. Photovoltage transients of the thin sample (90 nm thickness) at front and back side illumination.
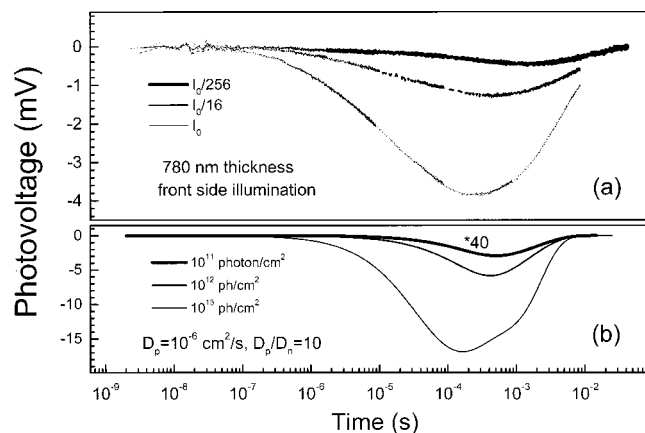

FIG. 4. Measured (a) and calculated (b) photovoltage transients of the thick sample for different illumination intensities.
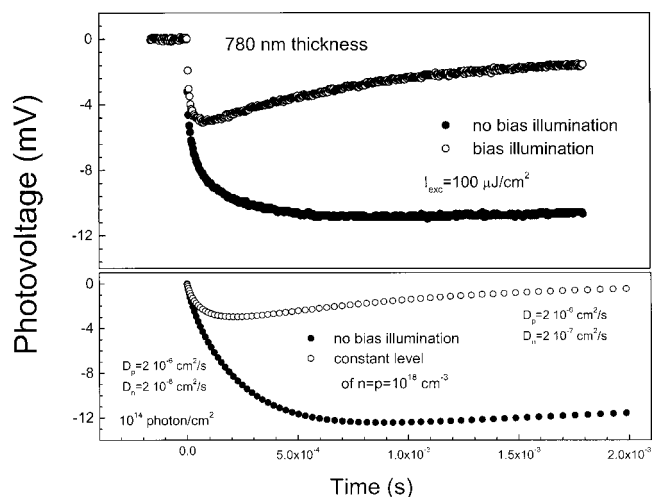
FIG. 5. Measured (a) and calculated (b) photovoltage transients of the thick sample for laser excitation with and without bias illumination.

allows us to estimate the values for D_p and D_n (D_p about 10^{-6} cm^2/s, D_n about $10^{-8} - 10^{-7}$ cm^2/s).

Figure 5(a) compares PV transients without and with cw bias light ($\lambda = 500$ nm, $I = 10$ mW/cm^2). These transients are shown in a linear time scale. The calculated PV transients are plotted in Fig. 5(b). The bias illumination was introduced into the model as a constant intrinsic concentration of electrons and holes.

The measured and calculated PV transients exhibit the same tendencies with changes of d and bias illumination. Some differences can be nicely seen on the linear time scale. The most striking difference is that the calculated PV transients increase slower than the measured PV transients. The reason for this is that due to the dispersive nature of the transport the diffusion coefficients decrease in time. This was not considered in our model. A second point is that t_{max} also decreases for the calculated PV transients under bias illumi-

nation. But one should increase the values of D_n and/or D_p to achieve a good agreement between experiment and simulation. This has a very important impact for device simulations. Of course, a more sophisticated model can give full data sets for D_p and D_n in PPV under different conditions.

IV. CONCLUSION

Finally, we showed that the PV method is a powerful tool for the investigation of charge carriers diffusion in PPV. The values of D_p and D_n are on the order of 10^{-6} cm^2/s and $10^{-7} - 10^{-8}$ cm^2/s, respectively, and increase at bias light illumination. The investigation of the diffusion PV can be also applicable to other materials with large τ_M.

ACKNOWLEDGMENTS

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