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Characterization of Fluorene - Thiophene Copolymer Layers by the Surface Photovoltage Method

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Summary: The surface photovoltage method was used for the study of thin polymer layers made of poly{(9,9-dihexylfluorene-2,7-diyl)[-3-(3-methylbutyl)thiophene-2,5-diyl]} prepared by spin-coating on ITO coated glass substrates. The surface photovoltage (SPV) in a thin polymer layer is a result of dissociation of photogenerated free excitons in electric field of the space charge region (SCR) which forms spontaneously at the surface. The photovoltage signal was formed between a transparent electrode capacitively coupled to the surface of the sample and the back ITO electrode. Photovoltaic spectra were measured under illumination both the free surface (SPV_{fs}) and the substrate (SPV_{ITO}) side and for various layer thicknesses. The shape of the SPV_{ITO} spectrum is very similar to that of the absorption spectrum, whereas the SPV_{fs} spectrum maximum is shifted to longer wavelengths. Fitting theory to the experimental data, the thickness of the space charge region and the diffusion lengths were evaluated. The results are discussed also in relation to photoluminescence study of thin films.

Keywords: conjugated polymers; diffusion length; fluorene-thiophene; surface photovoltage; thin films

Introduction

The use of semiconducting organic materials as an active layer in optoelectronic devices offers some advantages in processing and new possibilities of device fabrication. In molecular materials light absorption generates excitons, which must be dissociated in electric fields and electrons and holes transported to the electrodes. At the surface of materials a space charge region with internal electric field often spontaneously forms. This is employed in the surface photovoltage method yielding parameters essentially influencing solar cell operation. In this paper, a technique previously developed for inorganic materials is applied to an organic semiconducting polymer.

Preparation of the Fluorene-Thiophene (FlPT) Copolymer Layers

The synthesis and characterization of poly{(9,9-dihexylfluorene-2,7-diyl)[-3-(3-methylbutyl)thiophene-2,5-diyl]}, the structure of which is displayed in Scheme 1, are described elsewhere.[1] Thin polymer films were prepared by spin coating from tetrahydrofuran solutions. All solutions were filtered with 0.45 μm Millex-FH13 Millipore syringe filters prior to spin-coating. Thin films for optical studies were spin-coated onto fused silica substrates and for PV study onto indium-tin oxide (ITO) substrate. All polymer films were dried in vacuum (10^{-3} Pa) at 353 K for 1 h. Layer thicknesses were measured using a KLA-Tencor P-10 profilometer. UV-vis spectra were measured on a Perkin-Elmer Lambda 35 spectrometer and PL spectra using a Perkin-Elmer LS55 spectrofluorometer.

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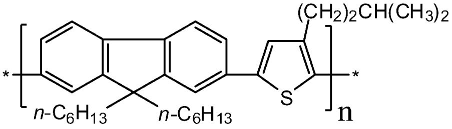

Scheme 1.

Principle of the Surface Photovoltage Method

The surface photovoltage (SPV) method is very useful for characterization of semiconducting materials.[2] It is non-destructive and the samples can be prepared without good ohmic contacts. The method has been widely used for determination of diffusion length L of minority charge carriers in inorganic semiconductors. Here, we use this technique for determination of exciton diffusion length in FIPT samples.

The schematic experimental arrangement is in Figure 1. The alternating voltage generated by the low-intensity monochromatic light chopped with a low frequency of 11 Hz is measured between a transparent conductive electrode capacitively coupled to the sample and an appropriate back electrode. The photovoltage generated in the FIPT layer is measured between the ITO substrate electrode and a second ITO electrode between which and FIPT layer a Mylar sheet serving as a dielectric layer was inserted. Free excitons generated in the bulk of thickness d diffuse to the SCR-bulk interface where dissociation into free electrons and holes occurs. Excitons generated in the SCR of thickness w are dissociated by its internal electric field. Both processes lead to the resulting photovoltage. The SPV measurement at various wavelengths brings information on the diffusion length of excitons in the bulk and on the SCR thickness. The SPV spectra were taken at constant impinging photon flux density and subsequently corrected for the transparency of the electrodes.

Theory

The surface photovoltage is generally:[3]

$$V = (nkT/e)\ \ln(1 + J/J_0) \tag{1}$$

where n is the ideality factor, J_0 is the saturated current density, J is the photogenerated current density and k, T, e have the usual meanings. The photogenerated current is formed both in the neutral bulk (thickness d) and in the space charge region (thickness w) at the free surface. In the case of the free surface illumination the component from the neutral bulk is calculated by solving the usual diffusion equation

$$\mathrm{d}^2\Delta p/\mathrm{d}x^2 - \Delta p/L^2 = -aI\ \exp(-a[w + x]) \tag{2}$$

where Δp is the concentration of photogenerated free excitons, L is their diffusion length, I is the intensity of radiation entering into the bulk with the absorption coefficient α. The boundary condition characterizing sweep of excitons at the bulk- SCR boundary is

$$\Delta p(w) = 0 \tag{3a}$$

The further condition means recombination at the bottom contact:

$$D\,\mathrm{d}\Delta p/\mathrm{d}x|_{x=w+d} = s\Delta p(w + d) \tag{3b}$$

where D is the exciton diffusion coefficient and s is the surface recombination velocity.

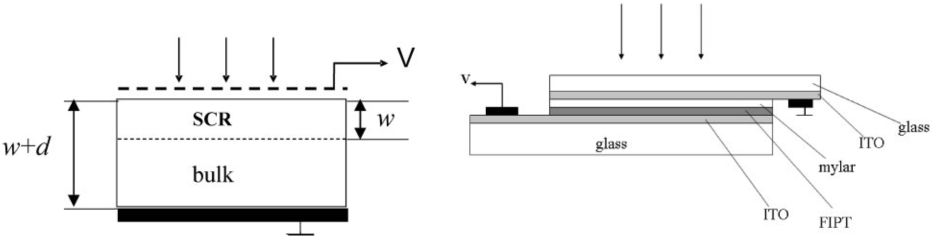

Figure 1.
Schematic arrangement of SPV measurement.

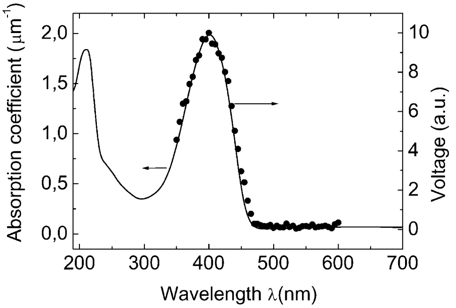

Figure 2.
Absorption spectrum (solid line) and the SPV spectrum (normalized to the same height) measured for the illumination from the ITO substrate side (solid circles).

Diffusion current density J_b from the bulk can be simply obtained as

$$J_b = eD\, d\Delta p/dx|_{x=w} \tag{4}$$

The component of the current density from the SCR is:

$$J_{SCR} = eIG(1 - \exp(-\alpha w)) \tag{5}$$

G is the gain factor characterizing losses by recombination in the SCR ($G \leq 1$). After inser-tion of $J = J_b + J_{SCR}$ into Eq. 1 the photovoltage V is obtained.[4] At low light intensity measurements V is proportional to the photocurrent J (Eq. 1). Similar calculation can be made if illumination comes from the substrate side.

Results and Discussion

Figure 2 shows absorption spectrum of the thin FIPT layer the shape of which is in accord with that of SPV spectrum measured under irradiation from the substrate side (SPV_{ITO}). The SPV_{ITO} signal is proportional to the absorption coefficient, which means that neither the diffusion length nor the surface recombination modifies the spectrum.

The SPV_{ITO} spectrum could be very well fitted by the theory outlined. Both SPV spectra measured from the substrate side (SPV_{ITO}) and under irradiation from the free surface (SPV_{fs}) are shown and compared with theory in Figure 3. A structure with a bulk region and only one SCR at its free surface is considered in the theoretical fitting. The presence of a further SCR, e.g. at the contact with the substrate, would lead to a sign change in the SPV spectrum, which was not observed. The theoretical fit (solid lines) revealed that the SCR spreads across a greater part (100 nm) of the polymer layer whereas the bulk region is very thin (25 nm). The SPV spectrum taken from the free surface side also confirms the presence of the thick non-efficient SCR layer. Weakly absorbed wavelengths penetrate deep into the material and generate a higher signal than the more absorbed wavelengths. This causes a shift of the SPV maximum to longer wavelengths. Measurements of FIPT

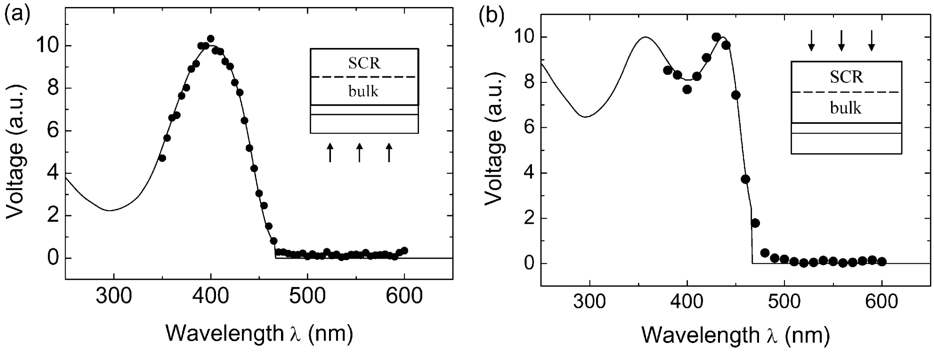

Figure 3.
Normalized SPV spectra (points) measured on a 125-nm FIPT layer under illumination (a) from the ITO substrate side and (b) from the top free surface side. Full lines are theoretical curves obtained as the best fit with $d = 25$ nm, $w = 100$ nm and $L = 20$ nm, $G = 0.01$.

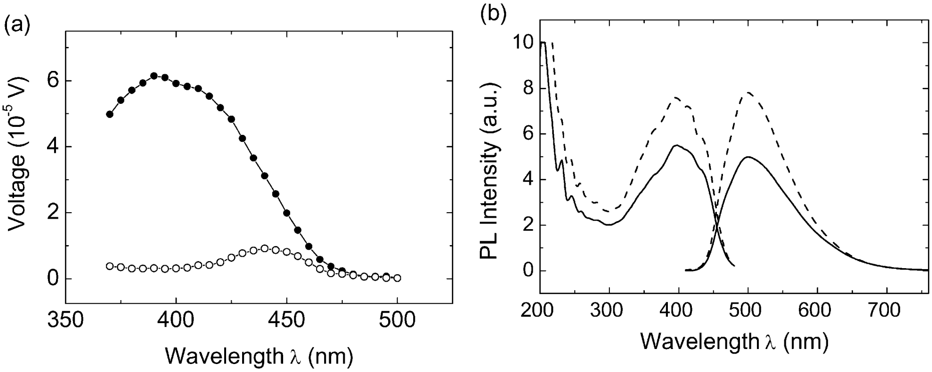

Figure 4.
(a) Absolute values of the SPV signal measured under illumination from the free surface side (open circles) and from the substrate side (solid circles). (b) Photoluminescence excitation and emission spectra of thin film measured from the free surface side (dashed) and the substrate side (solid). Emission wavelength 500 nm, excitation at 390 nm.

samples of various thicknesses did not indicate any thicker bulk region.

A low value of the parameter G brings about a high recombination rate in the SCR, which reduces the exciton lifetime in this region. A high recombination rate in the SCR results in a negligible contribution of this region to the SPV signal. This leads to a lower value of the SPV signal in the case of free surface illumination than that for the illumination from the substrate side as shown by the spectra in Figure 4a.

This is in good agreement with the photoluminescence study where a PL intensity measured with excitation and detection from the free surface side was higher than that measured from the substrate side (see Figure 4b).

Conclusion

The surface photovoltage method was utilized for the photophysical study of thin polymer FIPT layers. Photovoltaic spectra were measured for the illumination of the free surface and substrate side and could be well fitted by the SPV theory.[3,4] SPV measurements and a comparison of experimental data with theory revealed that only one space charge region is present. In a 125-nm layer, the 100-nm space charge region and 25-nm bulk region were evaluated and the diffusion length ca 20 nm was estimated. It was shown that the main contribution to the photovoltage comes from the bulk region due to a high recombination rate in the space charge region which results in its decreased contribution to SPV. These results are consistent with those of the photoluminescence study.

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