CONSTANT PHOTOCURRENT MEASUREMENT OF THE SUBGAP ABSORPTION IN POLYMER BLENDS

J. Willekens[*], T. Aernouts[a], G. J. Adriaenssens, J. Poortmans[a]

Semiconductor Physics Laboratory, University of Leuven, Celestijnenlaan 200 D, 3001 Leuven, Belgium
[a]IMEC vzw, Kapeldreef 75, 3001 Leuven, Belgium

The constant photocurrent method (CPM) was used to study sub-bandgap absorption in blends of the conjugated polymer MEH-PPV (poly [2-methoxy-5- [2'-ethyl-hexyloxy] -1,4-phenylene vinylene]) and the fullerene PCBM ((6,6) phenyl C61 butyric acid methylester) at different concentrations. The application of CPM to organic semiconductors is discussed in detail. It is argued that in these materials CPM leads to information about the product of the absorption coefficient and the quantum yield, which hampers the interpretation of the results.

1. Introduction

Over the last few decades, interest in organic semiconductors for optoelectronic applications has grown remarkably. This is mainly due to their economic advantages over inorganic semiconductors. In fact, it is the same qualities that make polymers so appealing in everyday use (flexibility, strength, light weight, ease of production and low cost) combined with semiconducting behaviour that make these materials so interesting. Applications include organic light emitting diodes, inkjet printed polymer transistors and solar cells. However, one of the main disadvantages for their use in photovoltaics is the high exciton binding energy, which leads to a high probability of exciton recombination and therefore a low photocurrent. A possible solution to this problem lies in the addition of a substantial quantity of fullerenes to the material, creating a polymer-fullerene blend. Because the electron affinity of fullerenes is large enough to compensate for the binding energy of the exciton, excitons can be broken by a charge transfer process in which an excited electron is transferred from the polymer to the fullerene.

2. Photocurrent in conjugated polymers

Photogeneration of free carriers in conjugated polymers is a complicated problem involving several steps. First, a singlet exciton is created, with a typical binding energy of 0.5 eV. Both carriers of the exciton then move in a potential well formed by their mutual Coulomb attraction and the external electric field. In the presence of a moderate electric field, the carriers still have to overcome a substantial potential barrier compared to kT. However, if the energy of the exciting photon is high enough, a Frank-Condon state is created above the $S1 \leftarrow S0$ transition. This state will relax vibronically to the $S1$ configuration, causing local heating of the chain on which the exciton is located. The effective temperature of the chain (T_{eff}) can then become sufficiently high for an activated jump over the potential barrier. It must occur on a very short timescale (~100 fs), since the

---

vibrational energy dissipates very fast. This process is called hot exciton dissociation [1]. It is obviously dependent on the electric field and the energy of the exciting photon. It also depends on the temperature of the material, since this determines the dissipation rate of the effective temperature. After hot exciton dissociation, a geminate pair with both carriers located on the polymer chain remains. The magnitude of the electric field and its orientation with respect to the chain determine whether the geminate pair recombines or whether free carriers are created.

Even if hot exciton dissociation does not take place and the exciton relaxes to the *S1* state, there is still a second way to overcome the potential barrier. As the exciton diffuses, it can dissociate at a charge transfer centre (CTC) whose electron affinity is sufficiently high to compensate the exciton binding energy. CTCs can be either intrinsic defects or dopants, such as the fullerenes used in polymer blends in order to increase photogeneration. This process is dependent on the energy of the exciting photon, since the exciton diffuses through the material by a series of Förster jumps to neighbouring sites on which the exciton can lower its energy. For pristine polymers, the dissociation probability is dependent on the energy of the exciting photon, because high energy excitons can find many sites on which they can lower their energy, compared to low energy excitons. For blends, the dopant concentration is normally so high that each exciton is created at a site neighbouring a CTC. After the dissociation, a geminate pair remains, with the hole located on the polymer and the electron on the CTC. The final step in the generation of free carriers involves breaking the geminate pairs. This is dependent on the external electric field and the Coulomb attraction between the electron and hole for pristine polymers [2]. For blends, the breaking of a pair is aided by the dipole layer at the interface of the polymer and the fullerene [3].

Transport in disordered organic semiconductors is described by a variable range hopping process in a Gaussian density of states [4]; holes being the majority carriers. It involves a Abrahams-Miller jump rate in which energetically-upwards jumps are activated and the jump rate decreases exponentially with distance. If a carrier is generated somewhere near the centre of the Gaussian density of states, it will relax through a number of predominately downwards jumps. As the carrier reaches the tail of the Gaussian distribution it will find fewer and fewer neighbouring sites with lower energy. Eventually it will have to make an upwards jump. It has been shown [5] that for a sufficiently steep DOS, a carrier localised at a deep tail state will most likely make an upwards jump to a site whose energy is near to a fixed value, the effective transport energy E_{tr}. The carrier can now again make a number of jumps until it is again trapped by a deep tail state. This process is highly reminiscent of multiple trapping transport in amorphous silicon. The effective charge carrier mobility , μ, is determined by the states near the effective transport level and the deep tail states.

Free carrier recombination is determined by the probability for free electrons and holes to meet. This implies that recombination is bimolecular and the recombination rate is proportional to the number of free carriers squared [6].

3. Constant phtotocurrent method in conjugated polymers

CPM measures the number of incident photons (N) required to keep the photocurrent fixed while different wavelengths (λ) in the absorption spectrum are scanned. From the value of N, information on the sub-bandgap absorption can be deduced. The photocurrent (I) can be written as

$$I = ph\mu\, F/l \tag{1}$$

p being the number of free holes, h the hole charge, F the electric field and l the distance between the electrodes. In the steady state, carrier generation is described by the following equation

$$\frac{dp}{dt} = G - Bp^2 = 0 \Rightarrow p = \sqrt{\frac{G}{B}} \equiv G\tau(p) \quad with \quad \tau(p) = \frac{1}{\sqrt{GB}} = \frac{1}{pB} \tag{2}$$

G is the free carrier generation rate, B is a constant describing bimolecular recombination, and τ the hole lifetime. The steady state generation rate is

$$G = N(1-R)(1-e^{-\alpha l})\eta \approx N(1-R)\alpha d\eta \tag{3}$$

in which N is the rate of incident photons, R the reflection coefficient, α the absorption coefficient, d the thickness of the material and η the probability that an exciton dissociates into free carriers (the quantum efficiency). The approximation made in the previous formula is valid for $\alpha d << 1$. Combination of equations (1), (2) and (3) leads to

$$I = N(1-R)\alpha d \eta \tau h \mu F/l \qquad (4)$$

The sub-bandgap value of R is independent of the wavelength [7]. A constant photocurrent at each wavelength implies a constant p and therefore a constant carrier lifetime. However, the quantum efficiency is strongly wavelength dependent in organic materials. Equation (4) then reduces to

$$\alpha(\lambda)\eta(\lambda) = constant/N(\lambda) \qquad (5)$$

During a CPM measurement in conjugated polymers, information about the product of the absorption coefficient and the quantum efficiency is obtained. Still, $\alpha\eta$ itself is an interesting parameter for material characterisation, as it is a measure of the number of absorbed photons that will lead to a contribution to the photocurrent. Because of the unknown constant in equation (5) extra information is necessary in order to scale the CPM results. This information can be found by extra measurements of photocurrent transients. Integration of the transient photocurrents determines the photogenerated charge, which is related to $\alpha\eta$.

4. Experimental details

The studied materials include MEH-PPV, PCBM and MEH-PPV:PCBM blends with (1:4), (1:1), (1:0.1) and (1:0.01) weight ratios. The materials were dissolved in chlorobenzene, and layers were formed by spin-coating on Corning 7059 substrates. The thickness of the films was around 100 nm. Gold contacts were vacuum evaporated on top of the film in a coplanar configuration with an inter-electrode gap of 0.5 mm. The CPM setup was a dc version, in which the light reaching the sample did not pass through a chopper and the photocurrent was measured with an ammeter. Lock-in detection was used to measure the intensity of the incident light. A dc field of maximum value $F=10^3$ V/cm was applied to the samples. For each sample, several CPM measurements were made and the data were averaged. The results are shown in Fig. 1. As mentioned above, no absolute values are obtained by CPM. In Fig. 1a the CPM results for different samples were multiplied by arbitrary constants in order to offset the individual curves. In Fig. 1b the results are scaled to an arbitrary value at 2.3 eV.
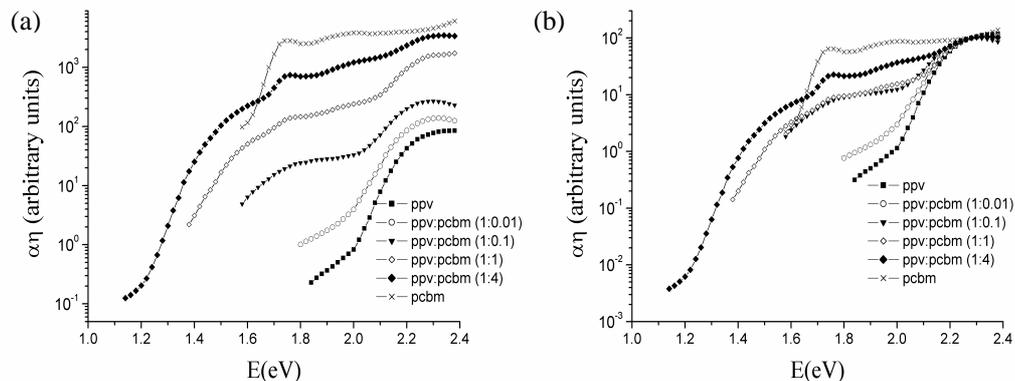

Fig. 1. CPM results for MEH-PPV, PCBM and the different blends.

The addition of fullerenes to MEH-PPV leads to a dramatic increase in the photocurrent, which implies that the CPM measurement can be made at considerably lower photon energies for

blends compared to pristine MEH-PPV. The broad peak in the absorption spectra of the blends at around 2.3 eV is obviously related to MEH-PPV. The peak at 1.75 eV, observed in blends with (1:4) and (1:1) weight ratios, stems from PCBM. For the pure MEH-PPV, and the (1:0.01) and (1:0.1) blends, an exponential rise is observed roughly between 2.0 and 2.2 eV. At even lower energies, a trailing off from the exponential form is seen. To a lesser extent and slightly shifted to higher energy, this rise is noticeable in the (1:1) and (1:4) blends. For PCBM, an exponential rise lies between 1.6 eV and 1.7 eV. In the (1:4) blend, an exponential rise is seen between 1.2 and 1.4 eV. The onset of this is also seen in the (1:1) and (1:0.1) blends.

5. Discussion

CPM spectra in organic materials are related to the $\alpha\eta$ product, which hampers interpretation of the results. The most simple assumption one can make about the absorption coefficients of blends is that they are superpositions of single component spectra. This has been verified many times (e.g. [8]) in the above-bandgap region of the spectrum. The fact that the positions of the MEH-PPV and PCBM related peaks in the blends do not shift in energy is an indication that this assumption is also valid in the sub-bandgap spectrum. However, it is argued [7] that the features below 1.6 eV in the CPM spectra of blends with high PCBM concentrations cannot be explained by a superposition of the spectra of their constituents, since no features are seen in the single component spectra at this energy. Therefore it is suggested that there is an interaction between the components, leading to absorption at lower energies. It is also argued in [7] that the trailing off from an exponential rise around 2 eV in the pristine material is a result of the dependence of the quantum yield to the Förster jump rate. Excitons created with energies below the inflection point are considered to be unable to find neighbouring sites of lower energy, and will therefore only have a small probability to dissociate at a charge transfer centre. Once the exciton energy is higher than the inflection point, the excitons are mobile and the dissociation rate increases dramatically. An alternative interpretation of the shift to lower energy in the CPM spectra of blends might involve the dependence of the quantum yield on the PCBM concentration. At low concentrations, the addition of extra charge transfer centres will enable excitons with increasingly lower mobility to find a CTC at which they can dissociate. As a result, the quantum yield will rise and shift to lower energies with increasing PCBM content. At high concentrations, the effect of the morphology of the blend on the quantum yield will become important [3].

6. Conclusions

CPM in organic semiconductors uncovers information about the product of the absorption coefficient and the quantum yield. Measurements were made on MEH-PPV, PCBM and different blends of MEH-PPV and PCBM. An explanation of the shift of the CPM spectra to lower energies in blends was suggested. This involves a shift in the quantum yield as opposed to a change in the absorption coefficient, as suggested in [7].

References

[1] V. I. Arkhipov, E. V. Emelianova, S. Barth, H. Bässler, Physical Review B **61**, 8207 (2000).
[2] V. I. Arkhipov, E.V. Emelianova, H. Bässler Chemical Physics Letters **372**, 886 (2003).
[3] V. I Arkhipov, P. Heremans, H. Bässler, Applied Physics Letters **82**, 4605 (2003)
[4] H. Bässler, Physica Status Solidi B **175**, 15 (1993)
[5] V. I. Arkhipov, E. V. Emelianova, G. J. Adriaenssens, H. Bässler, J. Non-Cryst. Solids **299-302**, 1047 (2002)
[6] P. W. M. Blom, M. C. J. M. Vissenberg, Mat. Sci. & Eng. R-Reports **27**, 53 (2000)
[7] L. Goris, K. Haenen, M. Nesládek, A. Poruba, M. Vanecek, P. Wagner, L. Lutsen, J. V. Manca, D. Vanderzande, L. De schepper, Submitted to Journal of Material Science.
[8] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, Science **258**, 1474 (1992).