

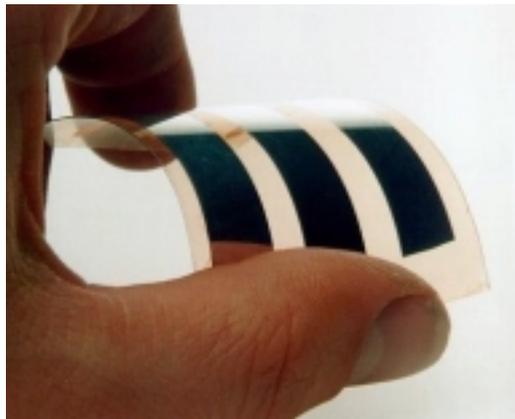
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POLYMER PHOTOVOLTAIC CELLS



polymer solar cell

Photovoltaic effect

- convert light into electric energy
- one of the photoelectric properties of semiconductor
- applications solar cell & photodiode (photosensor)

Contents

1. Experimental Tasks
2. Photoconductivity and Solar Cells
 - 2.1. Photoconductivity
 - 2.2. Solar Cells
3. Conjugated Polymer
4. Photovoltaic Devices Based on Conjugated Polymers
 - 4.1. General Considerations:
 - 4.2. Sandwich Devices
 - 4.3. Bulk Heterojunctions
5. Device Fabrication and Characterization
 - 5.1. Device Structure
 - 5.2. Device Characterization
6. Photovoltaic Polymers: Promising Prospect
7. Experimental Remarks
8. References

1. Experimental Tasks

- 1.1. Spectral calibration of optical setup with respect to irradiance and photon irradiance using different interference filters
- 1.2. Determination of IPCE efficiency as function of wavelength of two samples (pure and blended layer) for a constant photon irradiance
- 1.3. Determination of energy conversion efficiency as function of irradiance for a given fill factor
- 1.4. For discussion of action spectra and dependence of energy conversion efficiency on irradiance the absorption spectra and fluorescence have to be measured. The properties of both samples have to be compared.

2. Photoconductivity and Solar Cells

2.1. Photoconductivity

Semiconductors can be conductive with the help of light. The steps leading to photoconductivity are (Figure 1):

- a) If a photon has an energy $h\nu$ larger than the gap energy E_g , the photon is absorbed by the semiconductor and excite an electron (\bullet) from the valence band to the conduction band. The place in valence band, where the electron was removed, is called hole (\circ). The hole has a positive (plus) charge.
- b) In conventional semiconductors, the excited electron and the resulting hole migrate freely to opposite electrodes. **In a conducting polymer**, however, the electron and hole that are generated by the incident photon are bound into an **exciton** (Figure 2).
- c) Normally, these electron-hole pairs **recombine**, in part under emission of a photon, and the initial state will be obtained. But
- d) Under an **electric field** or **at interfaces**, these pairs can **separate** into **free electrons** and **holes**, which are **carriers** of electricity (**photocurrent**).

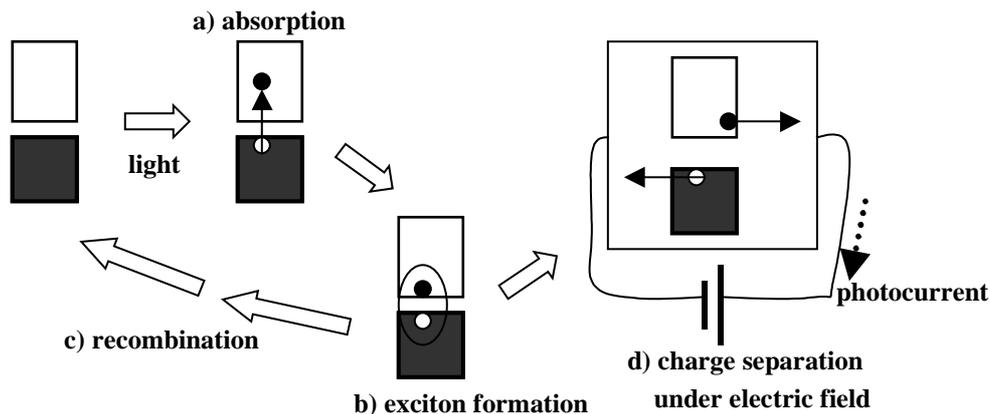


Figure 1: Steps to photoconductivity

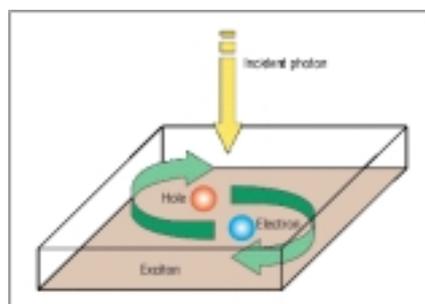


Figure 2: Excitons (bound electron–hole pair) are produced after light absorption in a conjugated polymer.

2.2. Solar Cells

While photodiodes work with an external bias, solar cells (photovoltaic cells) deliver electric energy without external bias. In order to obtain efficient conversion from light power to electrical power, the following steps need to be optimized:

- a) the fraction of light absorbed in the active region of the solar cell must be as large as possible,
- b) the generation of free carriers (photogeneration) after the absorption of photons must be large, implying the presence of an internal electric field,
- c) the generated carriers must reach the external circuit without any losses.

Most relevant parameters to describe the efficiency of conversion of light into electric current are:

the incident photons to converted electrons (IPCE) efficiency

$$\eta_{IPCE} = \frac{\text{number of electrons reaching the outside circuit}}{\text{number of incident photons}} ,$$

the power efficiency

$$\eta_E = \frac{\text{electrical output power}}{\text{total incident light power}} .$$

Ideally, η_{IPCE} and η_E are equal to one. Basically, η_{IPCE} can be written as a product of 3 terms:

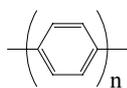
$$\eta_{IPCE} = A\eta_{CG}\phi_C$$

where A is the fraction of incident photons absorbed in the active region, η_{CG} the quantum efficiency of charge carrier photogeneration and ϕ_C the probability that the generated carriers reach the external circuit.

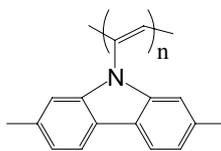
3. Conjugated Polymer

The main characteristic of conjugated polymer is the presence of a so called conjugated chain, where the chemical bonding between the atoms in the mainly carbon "backbone" of the polymer chain alternates between single and double bonds (Figure 3).

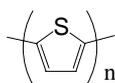
Single bonds are referred to as σ -bonds, and double bonds contain a σ -bond and a π -bond. The electron in a σ -bonds are strongly localized and form a strong chemical bond. In contrast, the electron in π -bonds are not localized and form much weaker bonds. As a result, the electrons in a π -bonds can be thought of as a cloud that extends along the entire length of the conjugated chain and in which the electrons are free to move along the molecules.



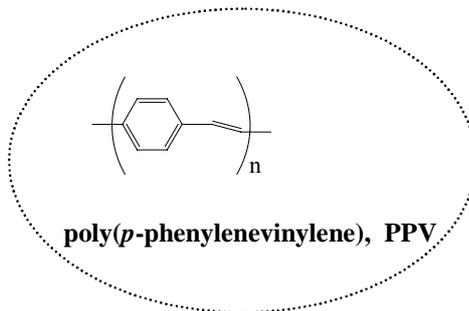
poly(*p*-phenylene)



poly(N-vinylcarbazole), PVK



polythiophene



poly(*p*-phenylenevinylene), PPV

- In π bonding, electrons **delocalize** to several atoms π bonding has **smaller E_g** than σ bonding.
- In conjugated polymers, electrons **delocalize** through the chain **decrease E_g**
semiconductive properties

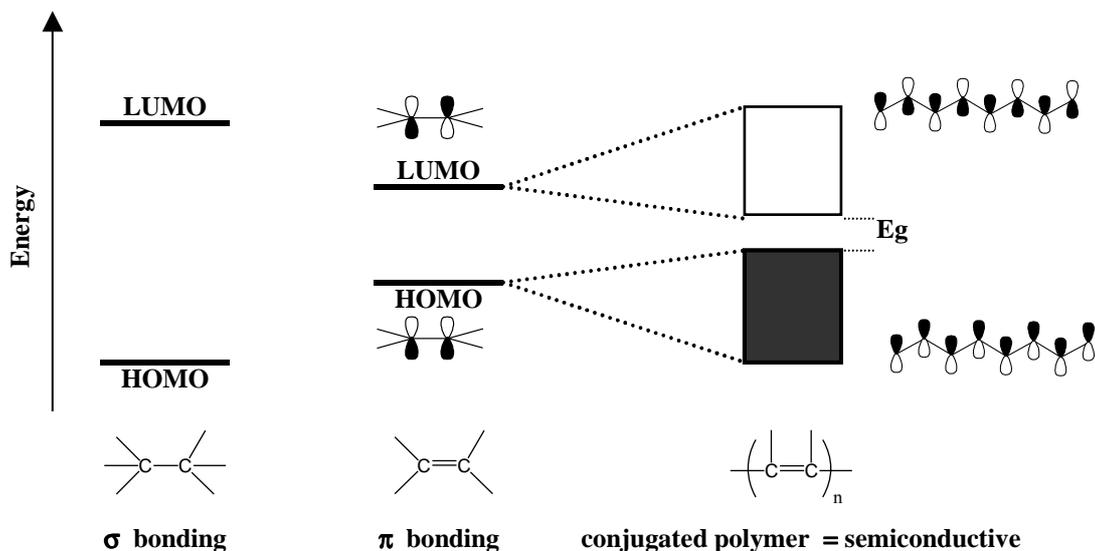


Figure 3

Most semiconducting polymers appear to have a band-gap that lies in the range 1.5–3 eV, which makes them ideally suited as optoelectronic devices working in the optical light range. Conjugated polymers can be used as the active material in a number of applications, including photovoltaic¹⁻³, light emitting diodes (LEDs)⁴⁻⁶, and field effect transistors (FETs)⁷, as the materials can easily be processed into thin film. Furthermore, the polymers are lightweight and flexible, with many of their properties being adjustable to suit specific requirements.

4. Photovoltaic Devices based on Conjugated Polymers

4.1. General considerations

Concerning photovoltaic applications, the following characteristics of conjugated polymers are most important:

- a) Polymers have sharp absorption peaks with very large absorption coefficients, such that a 200 nm thick polymer layer absorbs more than 90 % of the incident photons at the peak maximum (Figure 4).

thin layers ($d = 100 \text{ nm} - 200 \text{ nm}$) sufficient for effective light absorption.

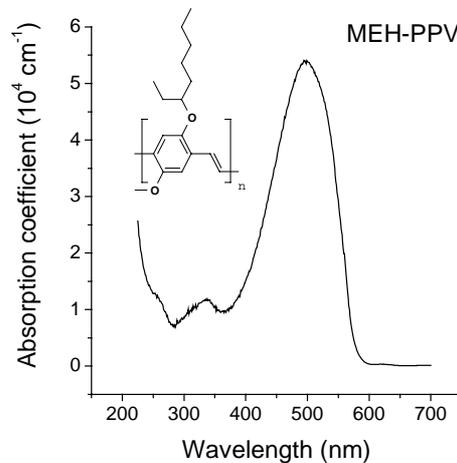


Figure 4: Absorption coefficient of solid MEH-PPV

- b) The photogeneration efficiency of pure conjugated polymers is strongly field dependent, due to the large binding energy of the excitons.

need large internal electric fields ($E \approx 10^7 - 10^8 \text{ V/m}$ equivalent 1 - 10 V per 100 nm) (Figure 5)

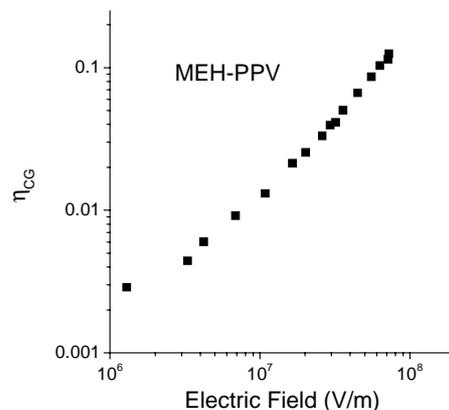


Figure 5: Quantum efficiency η_{CG} for photogeneration of charges as a function of the applied electric field for a thin layer of MEH-PPV

c) Pure conjugated polymers are mostly weakly p-doped, but n-doped polymers are rare.
 traditional pn junction photodiodes are not possible

4.2. Sandwich devices

A general approach to construct polymer solar cells is to sandwich a thin polymer layer of thickness d between two electrodes of different work function ϕ_1 and ϕ_2 (Figure 6).

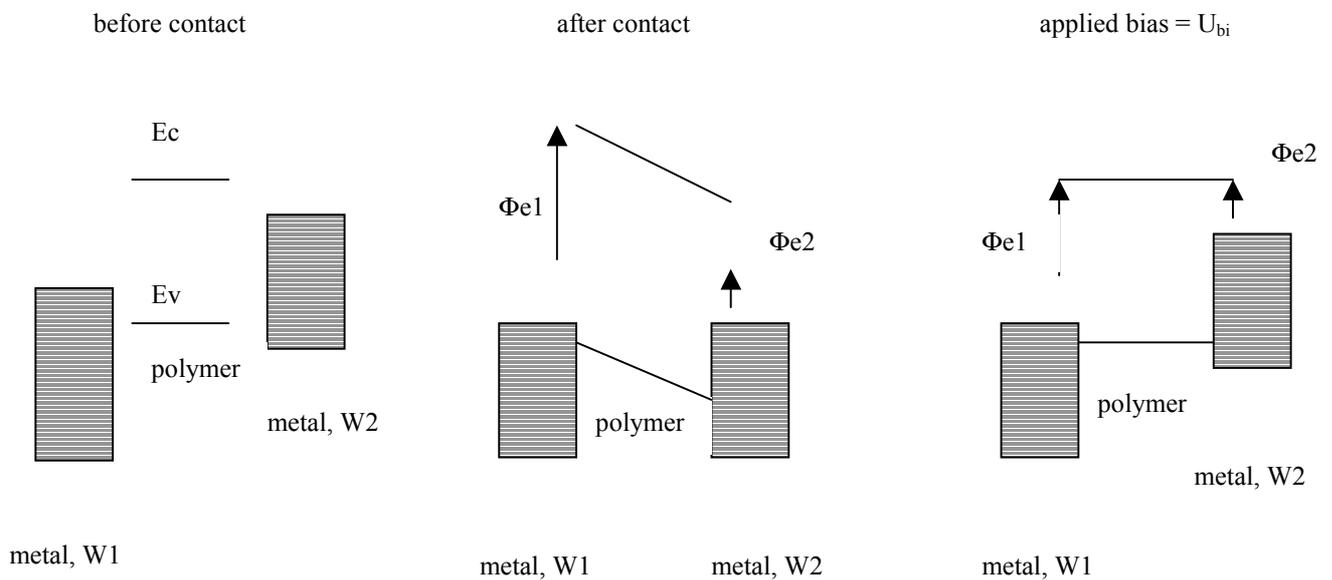


Figure 6: Schematic electron energy diagram of an electrode/polymer/metal sandwich device. Graphs show the structure before contact, after contact and after contact with a bias equal to build-in potential applied.

After contact, the Fermi-levels of the electrodes will become equal, resulting in an internal electric field

$$E_{bi} = \frac{\phi_{e1} - \phi_{e2}}{de} = \frac{\Delta\phi_e}{de}$$

and a build-in potential $U_{bi} = \Delta\phi/e = E_{bi} * d$. Here, e is the elementary charge. Typical electrode configurations are aluminium and ITO (indium tin oxide) with $U_{bi} \approx 0.5$ V and Al in combination with ITO covered by a conducting polymer layer (PEDT) with $U_{bi} \approx 0.9$ V.

When such a device is illuminated (without external bias), holes are collected at the high work function electrode (indium tin oxide, ITO) and electrons are collected at the low work function electrode (aluminum). Indeed, the open circuit voltage U_{oc} generated by these devices depends on the work function difference between the two electrodes. Indeed, if an external bias equivalent to the internal potential is applied, the internal electric field becomes zero and the generation efficiencies becomes small.

4.3. Bulk heterojunctions

Typical build-in fields for ca. 100 nm thick layers are in the range of 10^7 V/m, which results in values of η_{CG} of less than 1 % for pure bulk materials (see Figure 5). Attempts to improve the efficiency of the exciton-splitting led to the development of new conducting- polymer species that contained electron-donating (D) and electron-accepting (A) species. By creating an interface between polymers with differing electron affinities, it is possible to enhance the probability of exciton splitting via photoexcited charge transfer.

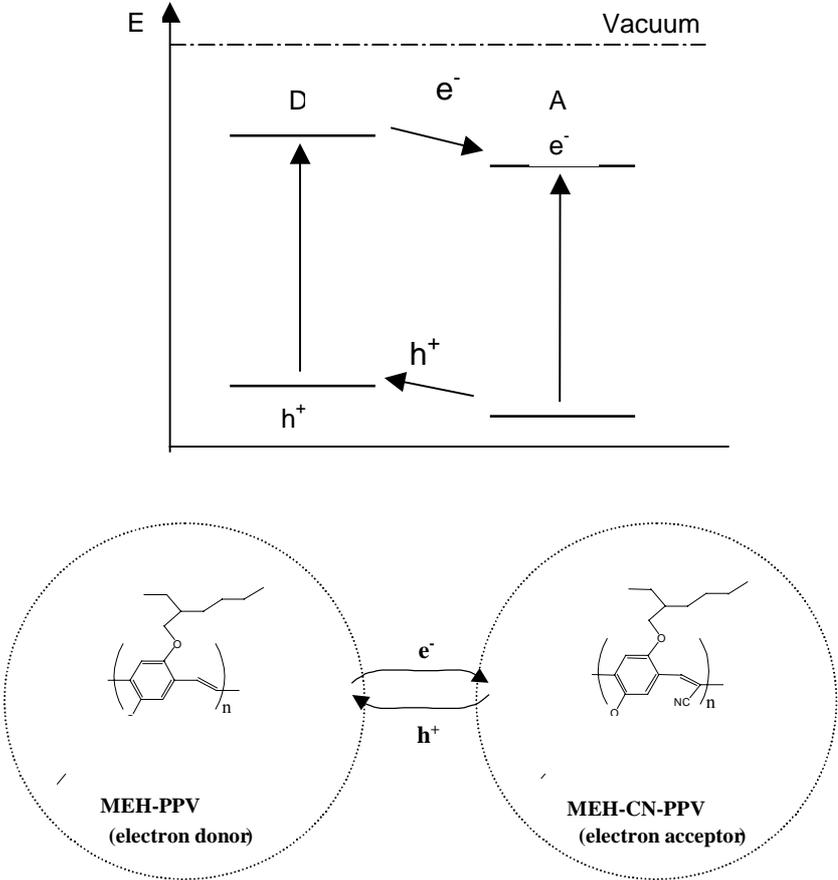


Figure 7: Photoinduced electron transfer between an electron-donating and an electron-accepting polymer

The simplest device configuration utilizing an electron-donating and an electron-accepting polymer is the simple bilayer structure shown in Figure 8. These heterojunctions work very well at separating excitons that arrive at the junction. Unfortunately, the lifetime of excitons is

short, and only excitons that are formed within ~ 10 nm of the junction will ever reach it. As the penetration depth of light is in the order of 100 nm, the short exciton diffusion range clearly limits the efficiency of these layered structures.

In an attempt to develop a more efficient photovoltaic structure, interpenetrating networks of electron-accepting (A) and electron-donating (D) polymers have been produced¹⁰. The simplest way to fabricate these structures are polymer blends of A with D. As a consequence of microphase-separation, the total D/A interface within the polymer layer will be greatly increased, and thus the probability that an exciton will encounter a junction and be separated will become larger.

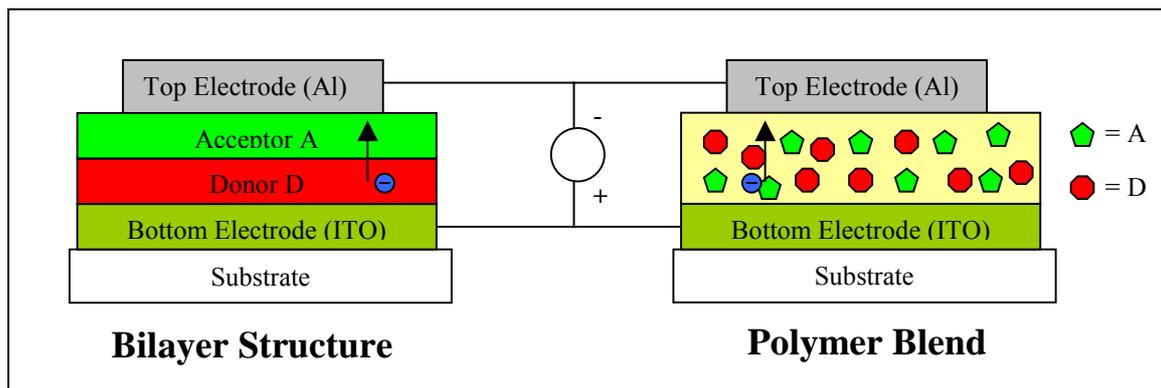


Figure 8: Layered structure and polymer blend structure based on an electron-donating and an electron accepting polymer

4.4. Spectral response¹³

Generally, the relationship between the optical absorption and the spectrally resolved photocurrent may be classified into two categories:

- a good correlation between the spectra so that the maximal photocurrent found for excitation at the peak of absorption spectrum is said to be sybatic
- if the maximum of photocurrent occurs for photon energies where the optical absorption is very weak (filter effect), then the correlation is said antibatic.

The antibatic behavior of thin film PPV cells is explained by different mobility of holes and electrons in PPV. The ITO/PPV interface is only contributing weakly to the photovoltaic properties. First, the ohmic interface at the ITO side is supposed to be rather ineffective in the charge carrier separation. Second, the low mobility electrons, photogenerated at the ITO side, have to pass the PPV bulk to reach the Al electrode. Both limitations do not occur on the PPV/Al interface. Due to the higher mobility of the holes compared to the electrons the positive carriers can reach the ITO electrode. The exact peak position of the photocurrent for antibatic conditions depends strongly on the thickness of the film. The best thickness is determined by absorption of most photons in a narrow region close to the Al electrode, where the generated electrons can reach the electrode. If the light is absorbed before this region (filter effect) the photocurrent is very small. The smaller the absorbance the more light comes into this region and can be absorbed. If the absorbance becomes too small much more light comes into the region but will not be absorbed.

5. Device Fabrication and Characterization

5.1. Device structure

A common configuration is illustrated in Figure 9. In general, ITO-coated glass was coated with the polymer by using spin coating technique, followed by drying (solvent evaporation) and deposition of Al as the electrode. For the samples used in the lab courses, the active area as defined by the overlap of the bottom and top electrode is ca. 1 cm^2

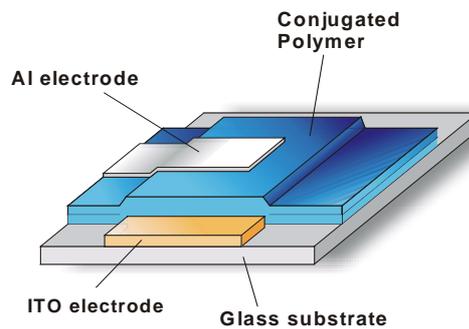


Figure 9. Photovoltaic device.

5.2. Device characterization

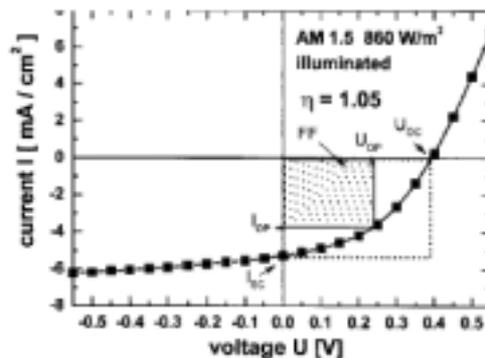


Figure 10. An example of current/voltage characteristics of photovoltaic device.¹¹

An example of the characteristic of the photovoltaic device is shown in Figure 10. The short circuit current (I_{sc}) is the current when the voltage is zero. The open circuit voltage (U_{oc}) is the voltage when the current is zero. The maximum output of the cell is given by the product $I_{op} \times U_{op}$, where I_{op} is the current and U_{op} is the voltage at the point where the solar cell delivers the maximum power. The values of I_{op} and U_{op} are obtained from the I vs U curve for the device where the product $I U$ is maximum at a point along the curve.

The fill factor (FF) is also important and is defined as:

$$FF = \frac{I_{op} U_{op}}{I_{sc} U_{oc}}$$

The fill factor is a measure, how much the $I U$ -curve resembles a rectangle. The smaller the consumption in the diode the higher the fill factor and the better the solar cell. The fill factor is always smaller than one. The fill factor can also be seen as the area ratio of the small rectangle in Figure 10 to the big dotted rectangle.

In addition, there are two measures of the conversion efficiency as mentioned above, namely the energy conversion efficiency η_E and incident photon to converted electron efficiency η_{IPCE} . In practice, η_{IPCE} is obtained as described below :

$$\eta_{IPCE} = \frac{hc \cdot J}{\lambda \cdot e \cdot E_E}$$

(h Planck's constant, c speed of light, λ wavelength, J photocurrent density, e elementary charge, E_E irradiance)

The energy conversion efficiency is related to the I_{sc} and U_{oc} via

$$\eta_E = FF \frac{I_{sc} U_{oc}}{\Phi_{E,ir}}$$

6. Photovoltaic Polymers and Promising Prospect

Conjugated polymers can exhibit electron–hole conduction similar to conventional semiconductors. Electrical currents are produced by separating the electron–hole pairs. This is done by forming interfaces between materials having different ionization potentials and electron affinities. Interfaces are created by superimposing layers of metals, and polymers. Although the best photovoltaic polymers produced so far are less efficient than their silicon counterparts, they produce much higher open-circuit voltages.

Polymers are being developed that use dyes to increase light collection efficiency. Polymerization methods are being developed that increase the structural order, producing more efficient charge transport properties. Perhaps one day, you can convert the outside of your house into one big solar collector using photovoltaic polymer paint.

Research into polymeric photovoltaics is at a very early stage, but the results are encouraging. The best materials produced so far, using a polythiophene molecule as a hole-acceptor (to enhance the absorption of sunlight), have an energy conversion efficiency of 7% when irradiated with green light and about 2% in sunlight³. Although these materials are currently much less efficient than their silicon counterparts, they do produce much higher open-circuit voltages. By using calcium anodes (which need to be capped to prevent oxidation in the atmosphere) and an ITO cathode, Grandstrom et al. obtained open-circuit voltages $>2\text{ V}^3$.

Silicon-based solar devices, on the other hand, have open-circuit voltages that are $<1\text{ V}$. The higher open-circuit voltages produced by the polymer-based devices mean that, compared with silicon cells, fewer polymer-based cells need to be cascaded together to obtain the same net output voltage. This may have significant advantages in certain low-power applications.

7. Experimental remarks

Polymer photovoltaic devices in this lab. course

Device 1. MEH-CN-Ether-PPV (A) with Al and ITO electrode (pure acceptor)

Device 2. Mixture of MEH-CN-Ether-PPV (A) and TPD-M3EH-PPV (D) with Al and ITO electrode (blend of acceptor and donor)

Both cells have an active area of $8 \times 12 \text{ mm}^2$.

UV/VIS absorption spectra

Measure the absorption spectra of an empty ITO-glass substrate as reference and subtract it from both the pure and the blend layer absorption spectra.

Fluorescence spectra

The fluorescence spectra will be measured using a modular spectrometer. Each part has a transmission characteristic. To obtain comparable spectra, these characteristics should be deleted using the so-called spectral correction function. Because you only want to compare both the spectra of pure and blended film, you do not have to correct them because they include the same mistake.

One correction you can perform easily is background correction (subtraction of dark signal) which is important for small signals. To do that, you measure the dark signal of the photomultiplier by closing the slit of excitation monochromator.

Calibration of optical setup

To produce a photocurrent you have to excite an exciton and separate it into an electron and a hole. For every such process you need a certain energy. At each wavelength, photons have different energies ($E_{\text{photon}} = h\nu$). Therefore, a certain light intensity (irradiance = light energy per time and irradiated area) does not correspond to the same photon irradiance (incident photons per time and area) for different wavelength.

Therefore, you need to determine the photon irradiance by measuring the intensity in dependence of lamp voltage for all filters used. Then, the photon irradiance is given by

$$E_p = E_E \cdot \frac{\lambda}{hc}$$

It is recommended to measure the filters from 350 nm to 600 nm.

Calibration of the setup must be performed before continuing with further tasks.

Photoaction spectrum (dependence of photocurrent on wavelength of irradiation)

Choose a photon irradiance of about $10^{14} / \text{cm}^2/\text{s}$ and then read the corresponding lamp driving voltage for each filter from the the lamp calibration graph. Then, measure dark and light short circuit currents for each wavelength after adjusting the lamp driving voltage. The difference gives the photocurrent.

Because higher currents can destroy the polymer film, you should not illuminate the cell for longer times.

Open circuit voltage

The open circuit voltage can be measured simply using a multimeter. You can measure it as a function of photon irradiance by adjusting the lamp driving voltage and calculating the photon irradiance with your calibration data.

Short circuit current as function of irradiance/ photon irradiance

As written before, the photocurrent depends on irradiance. To establish this dependence, measure the photocurrent (at irradiation wavelength of highest photocurrent) as function of photon irradiance. You set the photon irradiance by adjusting the lamp driving voltage and using your calibration data.

From the action spectra and the dependence of photocurrent on irradiance you can derive the incident-photon-to-converted-electron efficiency η_{IPCE} .

Lamp driving unit

The lamp's power supply has two outputs for up to 4 A each. The halogen lamp used needs 100 W, that is 8 A at 12 volts. To get these currents both outputs are connected parallel. Because at 4 A (that is one output completely opened, the other completely closed) the radiant flux is very low especially when using filters, it is recommended to leave one output opened all the time. Dark measurements then may be performed by shutting the way of light. All intensity measurements can be performed adjusting the second output. The power supply shows the correct voltage, the current of both outputs has to be added (that is 4 A plus the reading of the output adjusting).

Photo cell for light intensity (irradiance) measurements

The photo amplifier for calibration gives amplified voltages (0...10 V) to a multimeter. To get the real current flowing through the cell you multiply it by the amplification factor selected at the amplifier. The irradiance, that is the energy per time and cell's area (1cm²) is calculated using sensitivity from calibration table. Pay attention to the units given. If filter wavelength is not written in the calibration table, you may choose the closest one.

The bias switch at the amplifier must remain in the "bias" position (that is "off" position). The photon irradiance is the number of photons per time and area. You can calculate it by dividing irradiance by the energy of one photon.

Amperemeter MV 40

If you use the Amperemeter MV 40, you should be aware that there are two range switches. One (the lower one) you may call a "magnitude switch", it switches between micro, nano and pico Ampere. The second (upper one) switches in one range. A danger occurs if switching first to lowest range with the upper switch and then lowering the magnitude. In this case you switch for example from 1 μA to 1 nA, that is a difference of three orders of magnitude and will surely destroy the instrument. Make sure to switch first with the upper switch to 300 (highest range) and then change the magnitude.

Origin

All calculations may be done by using Origin. Type the measured independent and dependent values into columns and use other columns for calculations. Formulae are given by marking the column and choosing Column -> Set Column Values. You can plot data as graph by marking the desired column(s) and select Plot -> [Diagram type]. Before plotting you should make sure that the correct column is set for independent data, that becomes x axis (Column -> Set As -> X).

8. References

1. G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science* **1995**, 270, 1789-1791
2. J. H. Schön, Ch. Kloc, E. Bucher, B. Batlogg, *Nature* **2000**, 403, 408-410
3. M. Granström, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, R. H. Friend, *Nature* **1998**, 395, 257-260.
4. M. Gross, D. C. Muller, H. G. Nothofer, U. Scherf, D. Neher, *Nature* **2000**, 405, 661-665
5. M. Oda, S. C. J. Meskers, H. G. Nothofer, U. Scherf, D. Neher, *Synthetic Metals* **2000**, Vol. 111, 575-577
6. D. Sainova, T. Miteva, H. G. Nothofer, U. Scherf, D. Neher, *Applied Physics Letters* **2000**, 76, 1810-1812
7. Y. Yang, A. J. Heeger, *Nature* **1994**, Vol. 372, 344-346
8. G. G. Wallace, P. C. Dastoor, D. L. Officer, *Conjugated Polymers: New materials for photovoltaics*, *Chemical Innovation* **2000**, 30, 14-22
9. D. D. Leeuw, *Plastic electronics*, *Molecular Material, Physic World*, **1999** 31-34
10. J. J. M. Halls, C. A. Walsch, N. C. Greenham, E. A. Maseglia, R. H. Friend, *Nature* **1995**, 376, 498-500
11. C. Brabec, N. S. Sariciftci, J. C. Hummelen, *Advanced Functional Materials* **2001**, 11, 15-26
12. C. Brabec, N. S. Sariciftci, *Polymeric Photovoltaic Devices*, unpublished
13. C. Brabec, N. S. Sariciftci in: G. Hadziioannou, P.F. van Hutten (Eds.) *“Semiconducting Polymers: Chemistry, Physics and Engineering”*, Wiley-VCH **2000**