Materials Science-Poland, Vol. 22, No. 4, 2004

Polymeric photovoltaic devices

JANUSZ JAGLARZ[1], ADI KASSIBA[2], PAWEŁ ARMATYS[3],
MONIKA POKLADKO[1], EWA GONDEK[1], JERZY SANETRA[1*]

[1]Institute of Physics, Cracow University of Technology, 30-084 Cracow, Poland

[2]Laboratoire de Physique de l'Etat Condensé, Universite du Maine, 72085 Le Mans, France

[3]Faculty of Physics and Applied Computer Science,
AGH University of Science and Technology, 30-059 Cracow, Poland

We present a study on photovoltaic devices based on polypyrrole (PP) and SiC nanoparticles (~30 nm) in the matrix of poly(N-vinylcarbazole) (PVK). The photovoltaic cell structure was ITO/(polymer with SiC)/Ca/Al. The photophysics of such photoactive devices is based on photoinduced charge transfer from donor-type semiconducting conjugated polymers to acceptor-type SiC nanoparticles. The process mimics early photo effects in natural photosynthesis. In the general context of organic photovoltaics, polymeric materials have a cutting edge since they combine the photoelectrical properties of semiconductors with the large scale/low cost technology of polymeric materials.

Key words: *photovoltaic effects; polymer; photovoltaic cell*

1. Introduction

Organic photovoltaics, one of the first organic double layers reported in 1986 by Tang [1], only recently have become of broader interest. Organic materials, especially conducting polymers have been studied extensively owing to their potential application in active electronic devices [2, 3].

Polymer photovoltaics offer great technological potential as a renewable, alternative source of electrical energy. The potential advantages of an all-polymer heterojunction solar cell include: low cost (large scale production using the existing polymer processing technology), large area (plastic thin films can be produced with macroscopic dimensions), flexibility (the mechanical properties of polymers). The materials used are hydrocarbon-based non-toxic molecules, and the production of these thin film solar cells is done at room temperature without any dangerous exhausts. Since the band gap of polymeric semiconductors can be manipulated, it is possible to tune

---

[*] Corresponding author, e-mail: pusanetr@cyf-kr.edu.pl.

the colour of the solar cells, which in return is uniquely important for architecture. Furthermore, this approach allows unused large areas other than roofs to be accessed for photovoltaic energy conversion, by fabricating semitransparent photoactive thin films. These potential advantages bring a legitimate relevance for industrial interest to this approach.

Most of the development in polymer electronics has been done in the production of either p-n junctions or Schottky and metal-insulator-semiconductor diodes [4–6].

In spite of the intensively investigated photophysics of conjugated organic materials, the mechanism of charge carrier photogeneration is still under debate. The primary photoexcitations can be considered to be excitons that have a certain probability to dissociate into free charge carriers (polarons) (Fig. 1) if the binding energy of the exciton can be compensated [7]. There is a fast photoinduced charge transfer reaction in these polymer photovoltaic cells at the donor acceptor interface, which results in a metastable charge-separated state [8].

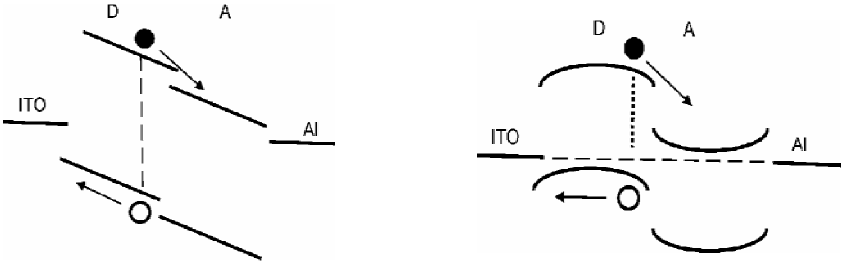

Fig. 1. Band energy diagrams for a D/A double layer device in the short circuit mode. Left: the built-in field, due to ΔW_f between the electrodes, leads to tilted bands if only a few free charge carriers are present. Right: at higher charge carrier concentrations, the bands can remain flat in the bulk, and blocking contacts may be formed [1]

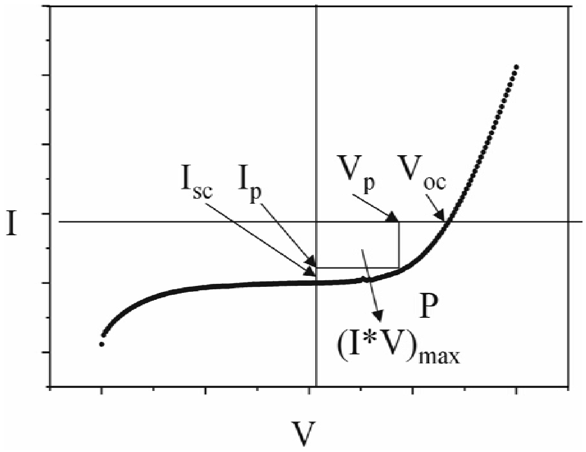

Fig. 2. The current versus applied voltage of a solar cell. The extracted current is negative. The fourth quadrant represents the voltage and current generated by the cell. An externally applied voltage is necessary to obtain data points in the first and third quadrant

The left figure in Fig. 1, shows a simplified band energy diagram for a double layer device with a low concentration of free charge carriers. The difference between the work functions of the electrodes ΔW_f can cause the bands to tilt, as shown, which creates a constant field across the bulk. The right figure in Fig. 1 shows the situation for a device with a free charge carrier concentration high enough to compensate the built in field within a fraction of the layer thickness. According to this picture, the driving force, i.e., V_{oc} is mainly determined by the offset at the D/A junction, although the increased built in field can help transport charges through the bulk.

The overall efficiency η_{eff} of a solar cell is calculated by the following formula:

$$\eta_{\text{eff}} = \frac{V_{oc} I_{sc} (FF)}{I_{\text{light}}} \tag{1}$$

where V_{oc} is the open circuit voltage, I_{sc} is the short circuit current in A/m^2, FF is the fill factor, and I_{light} is the incident solar radiation in W/m^2. The fill factor of solar cells, which reflects their diode properties, is determined by

$$FF = \frac{I_{mpp} V_{mpp}}{I_{sc} V_{oc}} \tag{2}$$

with I_{mpp} and V_{mpp} being the current and voltage at the maximum power point in the 4th quadrant of the I/V curve (Fig. 2).

2. Experimental

Semiconducting polymers can be used as electron donors in combination with SiC nanoparticles as electron acceptors to construct polymer photovoltaic cells.

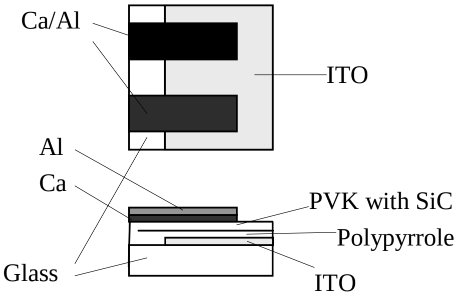

Fig. 3. Structure of the photodiode

Commercial poly(ethylene oxide)(poly(oxy-1,2-ethanedienyl), PEO, type Polyox WSRN 750, produced by Union Carbide, was used without further purification. Anhydrous iron(III) chloride ($FeCl_3$, Merck) was purified by sublimation. The PEO-

$FeCl_3$ (7:3) complex was prepared as described in [9]. Complex films were obtained by spin coating from solutions in nitromethane (10 wt. %). The polymerisation of pyrrole was carried out in the saturated monomer vapour at room temperature (21±2 °C). Thin polypyrrole composite films were prepared on the surface of the glass covered with ITO. Next, the tetrahydrofuran solution of PVK, used as a matrix of SiC nanoparticles (20–40 nm), was spin-coated on the polypyrrole layer (Fig. 3).

The chemical structure of the compounds is shown in Fig. 4. Calcium and subsequently aluminium as an electrode were evaporated on the surface.

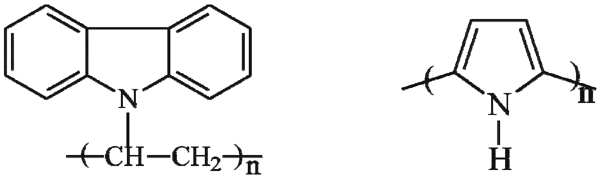

Fig. 4. Structures of poly(N-vinylcarbazole) (PVK) and polypyrrole (PP)

The photovoltaic cell had an active area of 0.3×0.5 cm^2. The structure of the cell, obtained this way, was ready to measure.

3. Results and discussion

First, an *I–V* characteristic of the structure was determined (Fig. 5), then the current in short circuit mode under light and voltage in open circuit were measured. Figure 5a shows the curves *I* vs. *V* of ITO/polypyrrole-PVK with SiC/Ca/Al structure in the dark, which exhibits a clear current rectification. Under illumination, the device exhibits a short-circuit current and an open-circuit voltage (Fig. 5b), which makes this structure a photovoltaic cell. Although it presents a very low current intensity, it is promising from the materials research point of view.

Figure 6 shows a schematic energy diagram of a PP and PVK with SiC heterojunction photovoltaic cell. The ionisation potentials of PP and PVK with SiC films were evaluated by photoelectron spectroscopy to be about 5.5 and 5.6 eV, respectively. The band gaps of PP and PVK with SiC were evaluated from the absorption edge to be about 3.2 and 3.0 eV, respectively. The work function of ITO [10] and Ca [11] were 4.6 and 3.2 eV, respectively. Since the conduction band of PVK with SiC is located about 0.2 eV below the conduction band of PP, electrons should be injected into PVK with SiC from PP at the PP/PVK interface by the dissociation of photoexcited excitons or exciton-polarons in PP.

It was assumed that the top of the valence band of PP is located at a higher energy than that of PVK with SiC by about 0.1 eV. This should make it possible to photoinduce hole transfer from PVK with SiC to PP in the same manner. That is, the photoinduced charge transfer by the dissociation of excitons and exciton-polarons results in

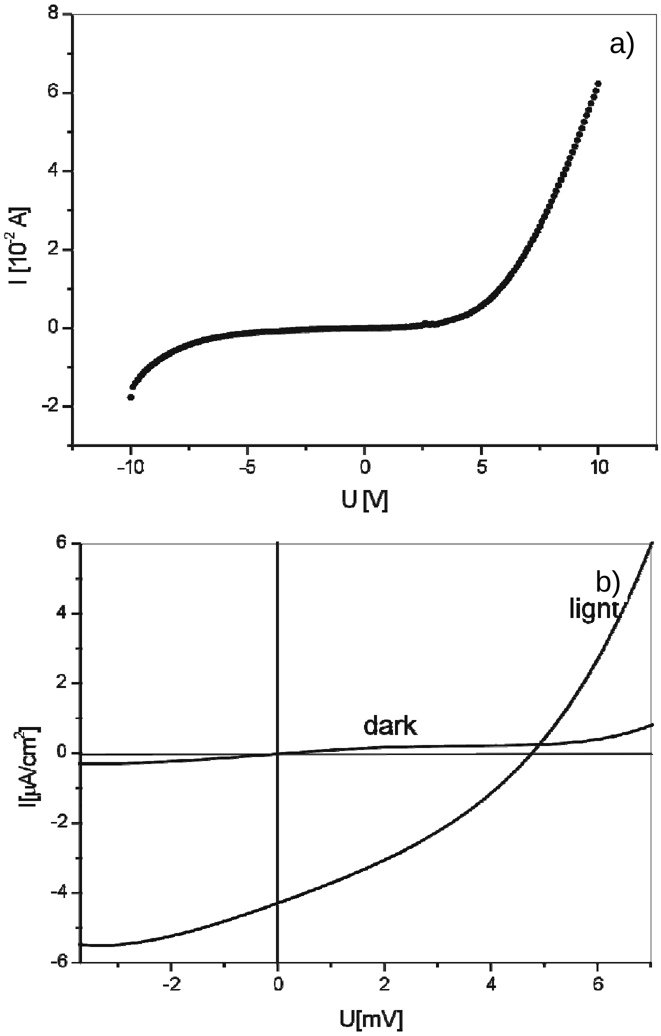

Fig. 5. Current density–voltage characteristics of an ITO/polypyrrole/PVK with SiC/CaAl cell: a) in the dark, b) in the dark and under 12 mW/cm^2 light irradiation

Table 1. Photovoltaic parameters for a sequence of layers

Sequence of layers	Short-circuit current density [µA/cm^2]	Open-circuit voltage [mV]	Power conversion efficiencies	Fill factor FF [%]
A) ITO/polypyrrole/PVK with SiC /Ca/Al	4.3	48	0.8 %	28
B) ITO/PVK with SiC-polypyrrole/Ca/Al	3.25	33	0.6 %	26
C) ITO/blend of polypyrrole and SiC/Ca/Al	0.25	167	0.2 %	17

the presence of positive carriers in PP and negative carriers in PVK with SiC. When the structure of the photovoltaic cell changes (ITO/PVK with SiC/PP/Ca/Al), the properties of the solar cell also change (Table 1). All characteristic photovoltaic parameters are smaller. The differences are not so large, because there is a small difference between the energy levels (Fig. 6) of the CB bands of PP and PVK with SiC. The same is true for VB bands, and is also caused of small values of V_{oc} for the investigated materials. In the case of structure C (Table 1), solar cells were built from a blend PP with SiC; their properties are different. The short circuit current is smaller than that for multilayer solar cells by one order of magnitude, but the open circuit voltage is higher.

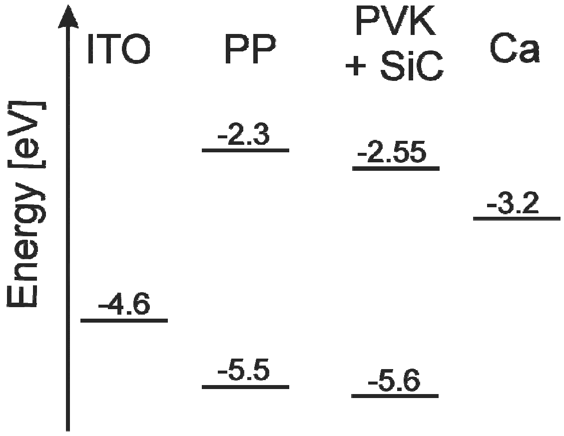

Fig. 6. Schematic energy band diagram of the ITO/PP/PVK with SiC/Ca/Al heterojunction photovoltaic cell

This effect is probably a result of the recombination of charge carriers and excitons in the bulk blend. Recombinations are caused by the migration of both negative and positive charges in the same material. This effect decreases the number of charges on the electrodes and sometimes increases the temperature of the cell.

4. Conclusions

Further optimisation of device performance can be achieved by optimising its physics:

- Optimising the choice of the D/A pair (energetics determine the open circuit potential). In addition, the band gap of the semiconducting polymer should be chosen for efficient harvesting of the solar spectrum.
- Optimising the network morphology of the phase-separated composite material for enhanced transport and carrier generation. The absorption of light and mobility of

the charge carriers within the components of the bulk heterojunction have to be maximized.

The photocurrent of the B) system photovoltaic cell (Table 1) is larger than that of the C) system photovoltaic cell by more than one order of magnitude.

The observed photoirradiation effects in the heterojunction photovoltaic cell can be explained in terms of photoinduced interfacial charge transfer between PP and PVK with SiC by taking into account the difference between the electronic states of PP and PVK with SiC.

Acknowledgements

This work has been partly supported by the State Committee of Scientific Research (KBN) in the years 2002–2005.

References

[1] TANG C.E., Appl. Phys. Lett., 48 (1986), 183.
[2] AKHMEDOV KH.M., KARIMOV KH.S., FIODOROV M.I., Appl. Sol. Energy, 31 (1995), 63.
[3] CHAMBERLAIN G.A., Sol. Cells., 8 (1983), 47.
[4] WORHLE D., MEISSNER D., Adv. Mater., 3 (1991), 129.
[5] CURRAN S., CALLAGHAN J., WLDON D., BOURDIN E., CAZINI K., BLAU W., WALDRON E., MCGOVERAN D., DALMESIERE M., SARAZIN Y., HOGREL C., Electron. Prop. Fullerenes, 117 (1993), 427.
[6] HAYASHI S., KOZARU K., YAMAMOTO K., Solid State Commun., 79 (1991), 63.
[7] ARKHIPOV V.I., EMELLIANOVA E.V., BASSLER H., Phys. Rev. Lett., 82 (1999), 1321.
[8] KRAABEL B., HUMMELEN J.C., VACAR D., MOSES D., SARICIFTCI N.S., HEEGER A.J., J. Chem. Phys., 84 (1996), 4267.
[9] RABEK J.F., LINDEN L.A., ADAMCZAK E., SANETRA J., STARZYK F., PIELICHOWSKI J., Mater. Sci. Forum, 191 (1995), 225.
[10] PARK Y., CHOONG V., GAO Y., HSHIEC B.R., TANG C.W., Appl. Phys. Lett., 68 (1996), 2699.
[11] MICHAELSON H.B., J. Appl. Phys., 48 (1977), 4729.

Received 14 September 2004
Revised 8 November 2004