Research proposal

1- Title of the project

Advanced parallel tandem structures for enhanced organic solar cell efficiencies

2- Applicant

Laaya Shaabani

3- Institute

Molecular Electronics - Physics of Organic Semiconductors (ME-POS)
Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4
9747 AG
Groningen
The Netherlands
Tel: +31 50 3634880
Fax: +31 50 3633900
L.Shaabani@student.rug.nl

4- Abstract

The growing need for energy by the human society and depletion of conventional energy sources demands a renewable, safe, infinite, low-cost and omnipresent energy source. One of the most suitable ways to solve the foreseeable world's energy crisis is to use the power of the sun. Photovoltaic devices are especially of wide interest as they can convert solar energy to electricity. Solar cells based on organic molecules and conjugated polymers are a good alternative for the conventional solar cells due to their potentially low manufacturing costs, their light weight and ease of processing but the low efficiency limits the use of them in industry. A tandem configuration is used to overcome the low efficiency limitation in organic cell devices. Tandem solar cells made from thermally evaporated molecules (Heliatek) already show efficiencies above 10%. We propose the development and characterization of

solution processed organic tandem solar cells which are easier to fabricate. This will lead to the development of cheap solar cells with higher conversion efficiencies.

In our project we use optical modeling that enables a fast and exhaustive numerical simulation of devices. This model can be used to exclude unfavorable parameter combinations for experimental devices and guide the search for new materials and techniques for improved designs. In this way the development of organic tandem solar cells with high performance will be accelerated.

5- Duration of the project

The project will start in September 2012. The duration of the project will be 4 years (until 2016) for the PhD student.

6- Details of Supervisors

Prof. Paul W.M. Blom
Room number: 5118.0005
Tel number: +31503634376
E-mail: p.w.m.blom@rug.nl
Paul de Bruyn
Room number: 5118.0015
Tel number: +31503635211
E-mail: p.de.bruyn@rug.nl

7- Cost Estimates

7.1 Personnel Positions

One ’onderzoeker in opleiding’ position for four years.

7.2 Running Budget

15 k€/year for conferences, summer schools and maintenance.

7.3 Equipment

No additional budget is required for equipment.

7.4 Budget Summery (in k€)

The expenses are summarized in the table below.

		2012	2013	2014	2015	2016	Total
Position	PhD Student	15	50	50	50	35	200
	Postdocs	-	-	-	-	-	-
	Technicians	-	-	-	-	-	-
	Guests	-	-	-	-	-	-
Costs	Personnel	15	50	50	50	50	200
	Running Budget	5	15	15	15	10	60
	Equipment	-	-	-	-	-	-
Total							260

8- Research Program

8.1 Introduction

Due to the depletion of fossil fuels, renewable energy sources such as solar and wind energies are of wide interest. Most solar cells are based on polycrystalline silicon and have a relatively high cost price determined by the costs of the starting material and the expensive manufacturing process. In the last years, the development of solar cells based on organic molecules [1–3] and conjugated polymers [4–6] has progressed rapidly which are a good alternative for the silicon-based solar cells due to their potentially low manufacturing costs and their light weight. One limiting parameter compared to more efficient, traditional silicon based devices is the low efficiency which limits the use of organic solar cells in industry. To make polymer based solar cells an economically interesting alternative the efficiency of these devices must be increased. One possible way to improve the efficiency is by using a tandem configuration in which two or more cells with different absorption spectra, i.e., different band gaps, are stacked. This increases the absorption of solar light and allows utilizing the photon energy more efficiently [7].

The organic or polymer “tandem cell” architecture is a multilayer structure that is equivalent to two photovoltaic cells, in which a transparent intermediate layer is positioned between the two active layers. This transparent intermediate layer provides electrical contact between the two cells via efficient recombination of the holes and electrons created in the different sub-cells without voltage loss.

The principle of a solar cell is shown in figure 1. Photons which are transmitted by a transparent electrode, are absorbed by the active material and excite the donor material, leading to the creation of excited electron–hole pairs (excitons). Excitons can relax back to the ground state by multiple pathways. One of the pathways is the route in which charge carriers are created. The created excitons diffuse within the donor phase until they encounter the interface with the acceptor. Dissociation then takes place via an ultrafast charge transfer (45 fs) from the excited donor to the acceptor, leading to charge separation. Subsequently, photo-generated holes and electrons are transported through the donor and acceptor phases towards the electrodes (anode and cathode) with the aid of the internal electric field, caused by the use of electrodes with different work functions. Finally they are collected by the electrodes, creating a current in the photovoltaic device.

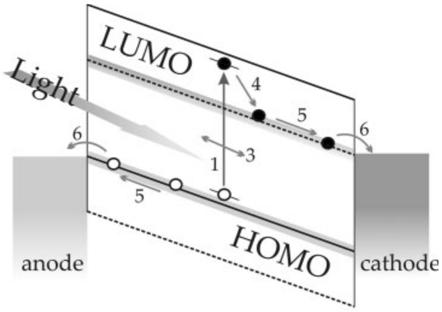

Figure 1: Principle of a polymer based solar cell. The incoming (sun) light is transmitted by a transparent electrode. The organic layer between the transparent and the metal electrode consists of a donor and acceptor material. Absorbed photons create an exciton on the polymer chain that can result in the formation of charge carriers (electron and hole). The charge carriers drift to the corresponding electrode creating a current. The dashed line represents the energy levels of the acceptor, while the full lines indicate the energy level of the donor in the PV cell. HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital[8].

8.2 Limitation of solar cell efficiency

Solar cell efficiency is limited by two main reasons: losses by thermalisation and non-absorption of low-energy-photons (Transmission loss). In the case of thermalisation, photons with energies larger than band gap of the semiconductor will lose their excess energy via thermal equilibration. For transmission losses, the energy barrier between HOMO and LUMO is too high for photon absorption and photons with energies smaller than the band gap cannot be absorbed. Figure 2a. illustrates this statement. Multiple junction (tandem) solar cells are used to improve the efficiency of organic photovoltaic devices. In this way, single heterojunction cells are stacked on top of each other to form a multilayer structure. One material should then collect the higher energetic photons and the other, with a lower band gap than the first one, should absorb photons with lower energy. The combination of a wide and small band gap polymer for a tandem solar cell improves use of photon energy and enables wider coverage of the solar spectrum.

8.3 The structure of an organic tandem solar cell

There are two methods to stack sub-cells: parallel or serial connections. The most common multi-junction solar cell employs a two terminal series configuration by stacking two active layers. The requirement for this configuration is just having thin, non-absorbing metallic or semiconducting layers to separate the different cells and act as recombination layer. See Figure 2b. For parallel connections, it is required to have intermediate electrodes which ensure efficient charge collection for each cell. In order to minimize photon losses and

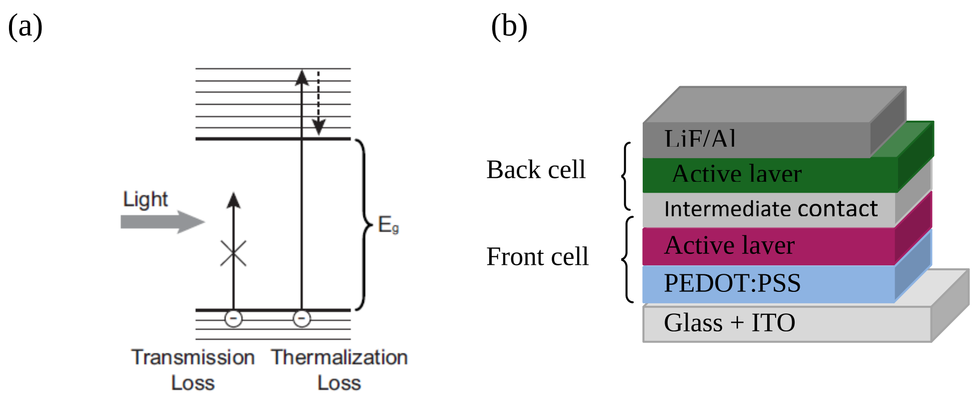

Figure 2: (a) Transmission loss and Thermalization loss. (b) Device structure of a polymer tandem solar cell.

maximize charge carrier collection, these electrodes have to be transparent and highly conducting. An obvious material for such electrode would be indium tin oxide [ITO]. However, ITO is usually deposited via reactive sputtering which might severely damage the conjugated polymer. Therefore, such parallel connections are not easily achievable in the case of organic semiconductor solar cells[9].

In the case of a series-connection, the intermediate layer acts as a recombination site, allowing holes from the HOMO of the back cell to recombine with electrons from the LUMO of the front cell. It consists of an electron transporting layer (ETL) in contact with the front cell and a hole transporting layer (HTL) in contact with the back cell. The energy band diagram of a polymer tandem solar cell is shown in Figure 3. The energy levels of ETL and HTL align with the LUMO of the front cell and the HOMO of the back cell respectively. Also, at the ETL/HTL interface, the Fermi levels align to avoid voltage losses. Upon light absorption, excitons are created in both photovoltaic cells. Then they dissociate at the donor - acceptor interface of each single cell. The electrons extracted from the front cell recombine with the holes collected from back cell at the ETL/HTL interface while holes from the front cell and electrons from the back cell are collected at the adjacent electrodes.

When the sub-cells are connected in series, the same current has to flow through the entire device (current matching). This current is limited by the lower current of the two sub-cells, which for organic semiconductors in most cases is the top cell. This means that the overall generated power is limited by the lowest generated power in the configuration. If one of the

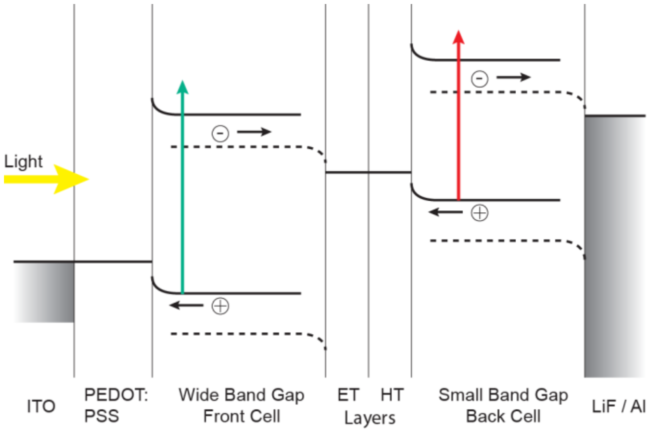

Figure 3: Energy band diagram of a polymer tandem solar cell under V_{oc} conditions

sub-cells generates much more current than the other, excess charges will be pile up at the intermediate layer and cannot contribute to the photocurrent. These charges generate an electric field and thus compensate for the built-in potential across the sub cell[10]. This compensation leads to a reduced fillfactor in the tandem cell[11]. To avoid such situations, optimization of the respective cell thickness has to be performed, which is a challenge[9]. With two sub-cells stacked in series, the voltage of a tandem cell is determined by the addition of the voltages of the sub-cells. In the case of a parallel connection, the short circuit current of the cells are summed up and the V_{oc} is driven by the smallest cell voltage.

In 1990, Hiramoto et al. reported on the first organic tandem solar cell by stacking two identical small molecule sub-cells (Me-PTC/H_2Pc). The two bilayer cells were separated by a thin layer (2 nm) of Au [12]. In 2002, Yakimov and Forrest presented the first multiple heterojunction solar cell with comparable small molecules (CuPc/PTCBI) stacking two, three, and five sub-cells in series which resulted in a very low current, but a doubling of the open-circuit voltage. Ultrathin (~0.5 nm) layers of Ag clusters were placed between the sub-cells to serve as recombination sites. [13]. In 2004, Xue et al. applied several modifications to the device structure and improved the device efficiency up to 5.7% by using a hybrid planar mixed heterojunction. They incorporated a blend of donor and acceptor molecules sandwiched between pure donor and acceptor layers[14]. In 2006, Dennler et al. made a hybrid tandem organic solar cell by stacking two different sub-cells with different absorption spectra. The first sub-cell was a heterojunction polymer solar cell based on a mixed layer of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM). The second one was composed of the small molecules zinc phthalocyanine:C60 (ZnPc: C_{60}). A layer (clusters) of 1 nm gold (Au) was used as recombination layer between the two sub-cells [15]. The first tandem cell composed of two polymer sub-cells was reported by Kawano et al. in 2005. They stacked two MDMO-PPV:[60]PCBM sub-cells and used spin casted PEDOT:PSS on a sputtered ITO layer as the intermediate layer[16]. In 2006, Hadipour et al. presented the first solution-processed organic tandem solar cell consisting of two bulk heterojunction sub-cells with complementary absorption spectra. The intermediate layer was a combination of evaporated metals[11]. Sista et al. introduced a device with a PEDOT:PSS/Au/ V_2O_5 middle contact in 2009[17].

8.4 Goal of the Proposal

In the proposed PhD project, we would like to fabricate, optimize, model, and characterize solution processed organic tandem solar cells which are more interesting because printing techniques are less time and energy consuming than thermal evaporation and eventually allow roll-to-roll production.

Polymers can be deposited from solution using simple methods such as spin-coating and slot-die coating. So, Semiconducting polymers are appropriate materials for developing low-cost technologies for large-area solar cells. There are several aspects that should be taken into account when fabricating tandem solar cells. The main difficulty of building a polymer tandem solar cell is creating a multiple layer structure without destroying or dissolving the underlying layers, especially when similar solvents are used. Therefore, it is important that an intermediate layer (middle contact) be thick enough to prevent impairment of the first active layer during spin coating (processing) of the second active layer. Another requirement is that this separating layer has to be as transparent as possible to transmit light efficiently to the second cell.

As a first step we consider a polymer tandem solar cell containing two sub-cells in a parallel configuration. This configuration generally is capable of producing higher currents and does not have the problem of optimization of the layer thickness of the sub-cells in a serial configuration. Therefore a parallel tandem solar cell can potentially lead to a higher performance compared to the tandem solar cell connected in series. Indeed, the V_{oc} of the parallel tandem cell is close to the V_{oc} of the front and back cells, while the current is equal to the sum of the photocurrents generated by both sub-cells. In the tandem solar cell structures the separating layer plays a very important role. The final efficiency of the tandem solar cell depends directly on the electrical (ohmic contact and proper conductivity) and optical (transparency) properties of this middle electrode[19]. In the parallel configuration, since the middle contact is used to extract the charges from the device, high sheet conductivity is a basic requirement.

Our device structure for a tandem solar cell with solution processed sub-cells is shown in Figure 4. The proposed geometry for this tandem cell is an inverted structure with P3HT:[60]PCBM as wide band gap front cell and a conventional structure with PCPDTBT:[60]PCBM as small band gap back cell. The complementary absorption band of the donor materials used for each sub-cell (P3HT and PCPDTBT) leads to coverage of the whole visible range of the solar spectrum (up to 900 nm). A drawback of the conventional device structure is that the ITO/PEDOT:PSS interface is unstable and has an adverse affect on organic device performance over time. One way of overcoming this drawback is using inverted devices utilizing an evaporated metal oxide/ metal anode (e.g. MoO_3/Al) instead of PEDOT:PSS which can leads to higher efficiency. An electrically conductive and transparent cathode should be placed on the ITO and a suitable anode should be placed on top of the active layer of the front cell. Thus, Zinc oxide (ZnO) as a low work function material can be used as a transparent cathode. We can use a simple, low temperature solution process to fabricate ZnO on the ITO layer. This process for the ZnO cathode involves spin casting and subsequent pyrolysis of the precursor material zinc acetylacetonate (Zn $(acac)_2$) hydrate. The next step of optimization to build up a tandem cell structure is the intermediate layer. As an anode, a transparent layer of molybdenum trioxide (MoO_3) can be used. Our preliminary results have demonstrated that we can propose a MoO_3/Ag/MoO_3 middle contact to separate and connect the two sub-cells. This layer serves as a hole transport (anode) and charge collecting layer for the first cell and at the same time as anode of the second cell. It serves as a stable foundation that enables the fabrication of the second cell to complete the tandem cell architecture. Then we can more precisely optimize the optical properties of the MoO_3/Ag/MoO_3 multilayer to achieve high conductivity and transparency. The quality, morphology and surface roughness of the separating layer can be analyzed by atomic force microscopy (AFM).

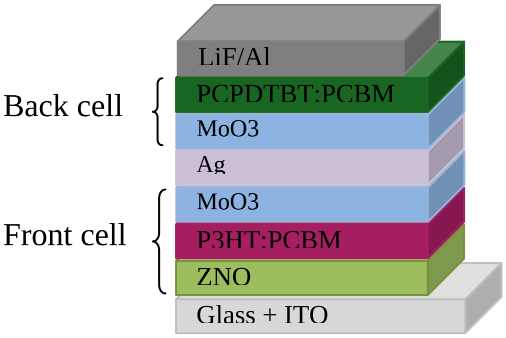

Figure 4. Device setup for a tandem solar cell with solution processed sub cells

A layer of PEDOT:PSS (work function ~5.2 eV) can be used to match the highest occupied molecular orbital (HOMO) of the donor PCPDTBT of the back cell. The PEDOT:PSS also improves the wetting for the processing of the active layer of the back cell. The outcome of this project will be very valuable to achieve better performance.

The project will also cover optical modeling. Theoretical analysis by optical modeling is a powerful mean to understand and predict optical effects and performance in organic solar cells. The optical constants (refractive index and extinction coefficient of each layer) and thickness of each layer which are needed for this modeling, can be obtained with variable-angle spectroscopic ellipsometry. By using the optical constants (real and imaginary parts of the complex refractive index $\tilde{n} = n + ik$, with n the refractive index and k the extinction coefficient) of each layer, we can describe the photon absorption profiles, transmission, reflection, and phase shift in various layers of the tandem cells.

The optical modeling will be done by a program developed in-house based on the transfer matrix formalism. This formalism describes the propagation of light through thin film layers and light refraction at a boundary between two media by using an elementary formulaic description in 2 by 2 matrices. These matrices can be multiplied with each other to yield simple 2 by 2 transfer matrices to describe a part or the whole layers. We can use the transfer matrix model to calculate the distribution of the intensity and absorption of light inside all layers. The light intensity $I(\lambda,x)$ can be calculated for each wavelength and position inside the entire layer, when the optical properties of each layer and the interference of light that is incident on the device with light that is reflected by the back electrode have been taken into account. By using the optical constants, the performance of tandem solar cells can be accurately predicted and efficiency can be optimized. The optical field at each position can be calculated with the resulting system transfer matrix. We can compare theoretical calculations using optical modeling with experimental results. This strategy provides a universal method to establish the optimal device layout and to further enhance the efficiency of future polymer tandem solar cells[21].

8.5 Plan of work

The plan of work is summarized in the following table. Of course, deviations from this scheme might occur due to unexpected problems or interesting findings might open different directions.

Time (year)	Activity
1st	Fabrication of several solution processed organic tandem cell devices, optimizing optical properties of middle layer and characterization
2nd	Optimizing organic tandem solar cells efficiencies and optical modeling of organic tandem solar cells
3rd	Determining how to produce the optimal device layout and enhance the efficiency further by using the results obtained from optical modeling
4th	Doing complementary experiments or new experiments if needed, PhD thesis writing

9- Infrastructure

This project is going to be carried out in the Molecular Electronics - Physics of Organic Semiconductors (ME-POS) Group at Zernike Institute. The infrastructure and facilities in the building of mathematical and natural sciences are adequate for the above mentioned project. For this proposed research we have the most important facilities:

- ✓ Cleanroom equipped with general processing facilities such as spin coating, thermal evaporator, optical microscope,…
- ✓ A four point probing bridge to measure the sheet resistance
- ✓ A Keithley 2400 SourceMeter for electrical characterization
- ✓ UV-VIS-near IR Absorption spectrometer for recording the absorption–transmittance spectra of the devices (optical condensed matter physics group)
- ✓ Atomic force microscope (AFM)
- ✓ Spectroscopic ellipsometry
- ✓ Optical microscope
- ✓ Quantum efficiency measurement system and solar simulator

10- Application perspective in industry, other disciplines or society

The growing need for energy by the human society demands a renewable, safe, infinite, low-cost and omnipresent energy source. Solar energy is especially of wide interest as it can be converted in one of the most useful forms of energy (electricity) by photovoltaic devices. Organic photovoltaic devices (OPVs) have received much attention due to their low-cost potential, light weight, and ease of processing. Development of solution processed organic tandem solar cells are promising developments towards higher efficiencies in photovoltaics.

11- References

[1] D. Wfhrle, D. Meissner, Adv. Mater. **3** (1991) 129.

[2] C.W. Tang, Appl. Phys. Lett. **48** (1986) 183.

[3] P. Peumans, A. Yakimov, S.R. Forrest, J. Appl. Phys. **93** (2003) 3693.

[4] S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromerz,, J.C. Hummelen, Appl. Phys. Lett. **78** (2001) 841.

[5] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science **270** (1995) 1789.

[6] C.J. Brabec, F. Padinger, N.S. Sariciftci, J.C. Hummelen, J. Appl. Phys. **85** (1999) 6866.

[7] J. Gilot, M. M. Wienk, and R. A. J. Janssen, Appl. Phys. Lett. **90** (2007), 143512.

[8] Blom P.W.M., Valentin D. M., L. Jan Anton Koster, and Denis E. Markov, *Adv. Mater.* ....(2007)

[9] Hans-Jürgen Prall, TANDEM SOLAR CELLS, PhD thesis, Johannes Kepler Universität Linz (2005).

[10] Jin Young Kim, et al., Science **317** (2007), 222.

[11] Hadipour A., de Boer B., Wildeman J., Kooistra F.B., Hummelen J.C., Turbiez M.G.R., Wienk M.M., Janssen R.A.J. and Blom P.W.M. *Adv. Funct. Mater.* ***16 (*** 2006), 1897.

[12] Hiramoto M., Suezaki M. and Yokoyama M. *Chem. Lett. (* 1990), 327.

[13] A. Yakimov, S. R. Forrest, *Appl. Phys. Lett.* ***80*** *(*2002), 1667.

[14] Xue J., Uchida S., Rand B.P. and Forrest S.R. *Appl. Phys. Lett.* ***85(*** 2004), 5757.

[15] Dennler G., Prall H.-J., Koeppe R., Egginger M., Autengruber R. and Sariciftci N.S. *Appl. Phys. Lett.* ***89*** *(*2006), 073502.

[16] K. Kawano, N. Ito, T. Nishimori, J. Sakai, *Appl. Phys. Lett.* ***88*** *(*2006), 073514.

[17] Sista S., Hong Z., Park M.-H., Xu Z. and Yang Y. *Adv. Mater. 22*, E77 (2010).

[18] Shaheen S.E., Radspinner R., Peyghambarian N. and Jabbour G.E. *Appl. Phys. Lett.* ***79*** *(2*001), 2996.

[19] A. Hadipour, B. de Boer, P. W. M. Blom, *Adv. Funct. Mater.* ***10*** *(*2007), 1002.

[20] D.J.D. Moet, M. Lenes, J.D. Kotlarski, S.C. Veenstra, J. Sweelssen, M.M. Koetse, B. de Boer, P.W.M. Blom, Org. Electron. **10** (2009) 1275

[21] Jan Derk Kotlarski, Optical and electrical modeling of polymer: fullerene bulk heterojunction solar cells, PhD thesis, University of Groningen (2012)