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THE INFLUENCE OF ABSORBING DONORS AND ACCEPTORS ON THE EFFICIENCY FOR A STACKED AND A MONOLITHIC ORGANIC TANDEM SOLAR CELL

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ABSTRACT: In order for organic bulk heterojunction solar cells to compete with the traditional inorganic cells, power conversion efficiencies of more than 10 % are desirable. A way to improve the efficiency is to use a tandem configuration. In this article, we study the influence of the energy levels (HOMO and LUMO) of donor and acceptor on the efficiency for a stacked and a monolithic organic tandem cell. First, we consider the case where only the donor of each subcell is the absorber active material. Then, we consider the situation where both the donor and acceptor are good absorbers; the photons absorbed in donor and acceptor are contributing to the output power of the solar cell. For our calculations, we always take into account the organic nature of the photovoltaic cell by imposing a minimal LUMO-difference, necessary for exciton dissociation. Ideal material characteristics are obtained from these calculations. They give us an idea how the configuration of the energy levels of the active materials should ideally be for stacked and monolithic organic tandem cells, and this for 2 situations: (i) only the donors absorbs light (ii) both donors and acceptors absorb light. One result is that the requirements for an almost optimal configuration for the stacked tandem cell are quite broad, permitting that the values of the bandgaps for optimal cells are not that strict. This is not the case for the monolithic configuration; especially the value of the bandgap E_{g1} of the first subcell is more critical than for a stacked cell. Another result is that when both materials absorb light, the highest maximum attainable efficiency reached is the same as in the case where only one material absorbs light, but higher efficiencies are reached for materials which have not optimal energy levels.
Keywords: modelling, organic solar cell, tandem.

1 INTRODUCTION

Photovoltaic solar cells based on organic compounds are promising candidates for solar energy conversion. They have the potential for cost effectiveness, mechanical flexibility and easy processing. Nowadays, efficiencies up to 5 % are reached [1]. However, in order to compete with the traditional inorganic cells, power conversion efficiencies above 10 % are a desirable. A characteristic of organic solar cells is their narrow absorption window compared to the absorption band of inorganic semiconductors. A possible way to use a wider band of the solar spectrum and thus increasing the power conversion efficiency, is using two solar cells with different bandgaps in a row, called a tandem solar cell. The absorber of the first single solar cell in such a tandem cell has a large bandgap E_{g1}. High-energetic photons with an energy $h\nu > E_{g1}$ are absorbed by the first cell and lead to a high useful output energy. The second cell, with a lower bandgap E_{g2}, absorbs the low-energetic photons with an energy between E_{g1} and E_{g2} (figure 1). In this configuration, the high-energetic photons still lead to a high output energy, but also the many low-energetic photons are absorbed. The single cells or subcells have of course a transparent front contact. The first cell has moreover a transparent back contact so that the light can penetrate into the second cell. The row can be extended with more single cells, i.e. a multi-junction solar cell.

Experimental and commercial tandem solar cells are usually of the monolithic (integrated or 2-terminal) type (figure 1b) because this type is easier to fabricate and apply. In a monolithic configuration, the subcells are not only optically in series, but also electrically in series. Through both single cells flows the same current. Therefore, a tandem cell of the monolithic type will never reach a higher efficiency as a stacked (4-terminal) tandem cell, because both single cells can't operate at the same time at their optimal working point (unless they have an equal maximum-power current).

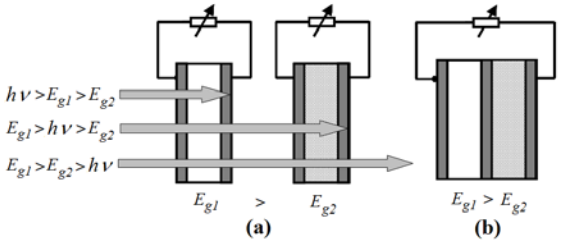

Figure 1: (a) A stacked or 4-terminal tandem solar cell: the first single cell absorbs photons with an energy higher than E_{g1}. The second cell absorbs photons with an energy between E_{g1} and E_{g2}. Photons with an energy below E_{g2} are not absorbed. The two subcells are electrically separated. (b) A monolithic or 2-terminal tandem solar cell: the single cells are electrically in series.

Organic tandem solar cells, where both single cells are organic solar cells, are already fabricated in several research institutes [2, 3], as well as full organic multi-junction cells [4]. The efficiency of these cells go hardly beyond the record efficiency of the single organic cell. Nowadays, efficiencies of more than 6 % are reached [5]. We already published articles in which we describe the influence of –among others- the energy levels on the efficiency of an organic solar (single junction and tandem) solar cell with one active material per (sub)cell [6, 7]. However, all these calculations were done for only a stacked configuration and only one absorber material per subcell: the donor (*p*-type) absorbs the light; the acceptor (*n*-type) not. In this article, we will describe the influence of two absorbing materials per subcell. Donor *and* acceptor are good absorbers and are contributing to the output power of the cell. We calculate the influence

of the energy levels for a stacked and a monolithic tandem cell. For our calculations, we always take into account the organic nature of the photovoltaic cell by imposing a minimal LUMO-difference, necessary for exciton dissociation. Ideal material characteristics are obtained from these calculations, giving an idea how the ideal organic solar cells should look like.

2 ASSUMPTIONS

The active material in a single organic bulk heterojunction solar cell consists of an interpenetrating network of an *n*-type (electron acceptor, e.g. fullerene derivatives) and a *p*-type (semi)conductor (electron donor, e.g. conjugated polymer), sandwiched between two electrodes with different work functions. The optical bandgap E_g is defined as the difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the absorber material. We consider a 4-terminal tandem solar cell, consisting of two single organic photovoltaic cells (figure 2 for the schematic energy band diagram). First, we assume that in each single cell, only one material absorbs the light. Usually, most light is absorbed by the *p*-type component and this is the case we will consider from here. In the other case, when the *n*-type material absorbs all the light, the results remain the same by permutation of *n* and *p* [6]. The organic cell with the widest absorber bandgap is in front (side of the sun), thus $E_{g1} > E_{g2}$. The distance between the HOMO of the *p*-type (donor) and the LUMO of the *n*-type (acceptor) is considered as the thermodynamic limitation for the useful energy [8]. We call this value the interface bandgap E_i.

For our simulation, the following fundamental assumptions are made for the stacked tandem cell (figure 1a): (i) every photon with an energy $h\nu$ higher than the bandgap E_{g1} is absorbed by the first cell and leads to a useful energy E_{i1}. This assumption means that the absorbed photon leads eventually to a free electron and a free hole, with an energy difference of E_{i1} between them. (ii) every photon with an energy $h\nu$ between E_{g1} and E_{g2} is absorbed by the second cell and leads to a useful energy E_{i2}. (iii) photons with an energy $h\nu$ lower than E_{g2} are fully transmitted. The maximum efficiency η_{max} is therefore given by (with $E_{g1} > E_{g2}$) :

$$\eta_{\max} = \frac{E_{i1}\int_{E_{g1}}^{\infty} N(E)\,dE + E_{i2}\int_{E_{g2}}^{E_{g1}} N(E)\,dE}{\int_{0}^{\infty} E\,N(E)\,dE}$$

with $N(E)$ the incident photon flux. For all our simulations, we use the AM 1.5 experimentally measured solar spectrum [9]. Notice that the denominator is the incident photon power density of the solar spectrum and does not depend on any bandgap. In this ideal scenario, the open circuit voltage V_{oc} of the first and second subcell will respectively be given by E_{i1}/q and E_{i2}/q. The fill factor *FF* of both subcells equals unity, as well as the quantum efficiency *QE* of the first cell for wavelengths lower than the cut-off wavelength λ_{g1} (corresponding with E_{g1}). The *QE* of the second cell equals unity for wavelengths between cut-off wavelength λ_{g1} and λ_{g2} (corresponding with E_{g2}).

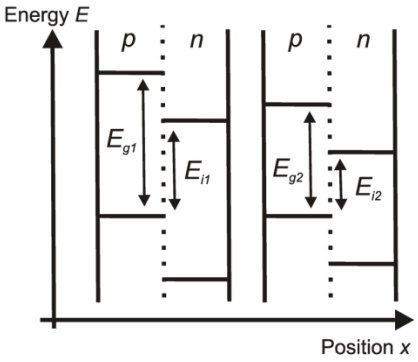

Figure 2: The schematic energy band diagram of a stacked organic tandem solar cell. The mutual position of the single cells does not matter, because the cells are only optically and not electrically in series. The absorber bandgap E_g and the interface bandgap E_i of each subcell are indicated.

In a monolithic or integrated tandem solar cell (figure 1b), the individual cells are electrically in series. This means that the total voltage over the cell is the sum of the voltages over each individual cell, and thus is equal to the sum of the interface bandgaps of both single cells. Also, through both single cells flows the same current. Hence, the maximum efficiency η_{max} for a monolithic organic tandem cell is given by (with $E_{g1} > E_{g2}$):

$$\eta_{\max} = \frac{(E_{i1} + E_{i2}) \cdot \min\left(\int_{E_{g1}}^{\infty} N(E)\,dE,\ \int_{E_{g2}}^{E_{g1}} N(E)\,dE\right)}{\int_{0}^{\infty} E\,N(E)\,dE}$$

with $\min(x,y)$ the minimum of x and y. The open circuit voltage V_{oc} of the whole monolithic tandem cell will be given by $(E_{i1}+E_{i2})/q$, the fill factor *FF* equals unity, as well as the quantum efficiency *QE* for wavelengths lower than the cut-off wavelength λ_{g2}.

In most organic solar cells, it is mainly the donor (*p*-type) who absorbs most of the light. The contribution of the absorbed light by the acceptor (*n*-type) to the power output can be neglected. However, fundamentally, there is no reason the *n*-type couldn't also contribute to the absorption of photons, if appropriate materials could be found and synthesized. In this (theoretical) case, the *p*-type should act as a "hole acceptor" for the holes created in the *n*-type. This is possible if the HOMO level of the *p*-type is higher than the HOMO level of the *n*-type. We now study if the efficiency of an organic tandem cell can be improved by also using the acceptor as an "active absorber". Hence, we now consider the case where not one, but both the *n*- and *p*-type material in each subcell absorb light. All photons with an energy higher than $E_{g,n}$ or $E_{g,p}$ will ideally be absorbed. Every absorbed photon still leads to a usefull energy $E_{g,i}$. Therefore, the maximum efficiency η_{max} is for a stacked configuration given by (with $E_{g1} > E_{g2}$):

$$\eta_{\max} = \frac{E_{i1}\int_{\min(E_{gp,1},E_{gn,1})}^{\infty} N(E)\,dE + E_{i2}\int_{\min(E_{gp,2},E_{gn,2})}^{\min(E_{gp,1},E_{gn,1})} N(E)\,dE}{\int_{0}^{\infty} E\,N(E)\,dE}$$

and for a monolithic configuration by:

$$\eta_{\max} = \frac{(E_{i1} + E_{i2}) \cdot \min\left(\int_{\min(E_{gp,1}, E_{gn,1})}^{\infty} N(E)\,dE, \int_{\min(E_{gp,2}, E_{gn,2})}^{\min(E_{gp,1}, E_{gn,1})} N(E)\,dE \right)}{\int_{0}^{\infty} E\,N(E)\,dE}$$

In organic bulk heterojunction solar cells, light absorption does not lead immediately to free charge carriers, but an exciton is created. In an ideal scenario, the highest efficiency is reached when the LUMO of the *p*-material is as close as possible to the LUMO of the *n*-material [6]. However, a necessary condition for efficient dissociation of the created excitons is that the difference between the LUMO's of the donor and acceptor is higher than the exciton binding energy. Thus, without a sufficient energy difference between the LUMO's of both materials, the solar cell cannot work. The value of the exciton binding energy in different materials is a subject of discussion, and values in a large range from 0.1 eV to 2 eV have been published [10]. The excess of this necessary minimum of the LUMO-difference corresponds with an energy loss. Each additional difference of 0.1 eV between the LUMO's results approximately in an additional 10 % relative efficiency loss in the maximum attainable efficiency. In the following calculations, we assume for the organic solar cell a difference of 0.2 eV between the LUMO's. This value was put forward as an empirical threshold necessary for exciton dissociation [11]. Only because of this necessary energy difference between the LUMO's, the attainable efficiency for the organic bulk heterojunction tandem solar cell drops 16-17 % relative in comparison with their inorganic counterpart, purely because of the difficult exciton dissociation.

3 RESULTS

Figure 3a and 3b show respectively the maximum efficiency in the ideal scenario for a stacked and monolithic organic tandem cell with donor bandgaps E_{g1} and E_{g2}, a full absorption window for the subcells and a LUMO difference of 0.2 eV between *n*- and *p*-type, characteristic for organic solar cells. A maximum efficiency of respectively 54.0 % and 53.3 % is reached for a stacked and monolithic tandem cell. As already mentioned, the efficiency of a monolithic configuration will never be higher than a stacked configuration. Comparing with a single junction organic cell [6] with an optimal bandgap of 1.1 eV, adding a second subcell results in a relative gain of about 1/3 in power conversion efficiency. The higher the bandgap, the less photons are being absorbed from the solar spectrum, but the higher the useful output energy of each absorbed photon. Hence, there is an optimum for each bandgap. This maximum occurs for the stacked and monolithic tandem cell respectively at a configuration (E_{g1}, E_{g2}) of (1.7 eV, 0.9 eV) and (1.6 eV , 0.9 eV).

The requirements for an almost optimal configuration are for the stacked tandem cell quite broad, permitting that the values of the bandgaps for optimal cells are not that strict. This is not the case for the monolithic configuration; especially the value of the donor bandgap E_{g1} of the first subcell is more critical than for a stacked cell.

Most organic absorbers have a wide bandgap and the production of suitable organic absorbers for photovoltaic applications with a narrow bandgap is a problem [12]. If we suppose an organic cell with bandgaps E_{g1} = 2.5 eV and E_{g2} = 1.5 eV, the stacked cell still has a maximum efficiency of 43.6 %, whereas the monolithic cell only reaches 22.4 %. The monolithic tandem cell is much worse than the stacked cell for non-optimal bandgap configuration. For an optimal bandgap configuration however, the difference is negligible. This means that for the production of tandem cells, the choice of good bandgap combinations (and thus material combinations) is much more limiting for a monolithic configuration as for a stacked configuration. The reason for the inferior performance of monolithic cells for non-optimal bandgap configurations is that, if the two subcells are stacked in series, the current which can be extracted from the tandem cell will be the lowest of the currents generated in the subcells. This means that the extracted current of the tandem configuration is almost the same as the photocurrent of the subcell that generates the lowest current. If one subcell generates much more current than the other subcell, the excess of charge carriers cannot recombine at the intermediate contact between the subcells. This will cause a charging at the intermediate contact and will partially compensate the built-in voltage across the other cell until the current of both subcells matches. This will lower the power conversion efficiency. Only when both subcells operate at their optimal working point, i.e. generate more or less the same current, the efficiency of the tandem configuration is optimal. Current matching is therefore necessary in a monolithic configuration. This explains why any choice of bandgap configuration where the subcells generate too different currents, will decrease the efficiency seriously compared with a stacked tandem cell.

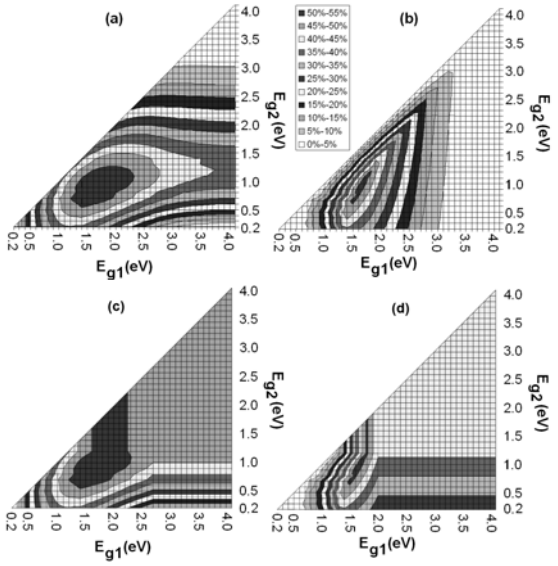

Figure 3: The maximum efficiency η_{max} in the ideal scenario for organic tandem cell with donor bandgaps E_{g1} and E_{g2} and a LUMO difference of 0.2 eV between *n*- and *p*-type. (a) A stacked cell where only the donors absorb light. (b) A monolithic cell where only the donors absorb light. (c) A stacked cell with absorbing donors and acceptors; E_{gn1} = 2.7 eV, E_{gn2} = 1.2 eV. (d) A monolithic cell with absorbing donors and acceptor; E_{gn1} = 2.0 eV, E_{gn2} = 1.2 eV.

We now consider the case where not one, but both the *n*- and *p*-type material in each subcell absorb light. Figure 3c and 3d show respectively the maximum efficiency in the ideal scenario for a stacked and monolithic organic tandem cell with donor bandgaps E_{g1} and E_{g2} and absorbing acceptors. As example, we choose the bandgaps (E_{gn1}; E_{gn2}) of the acceptors respectively (2.7 eV; 1.2 eV) and (2.0 eV; 1.2 eV). All calculations take into account the organic nature of the solar cells, by imposing a minimal LUMO-difference as described above. Two regions are present. In the region where $E_{g,p}$ of one subcell is the smallest of the two bandgaps in a subcell, the efficiency is the same as the case with only one material absorbing. In the region where $E_{g,n}$ is the smallest, the efficiency is now higher, because the *n*-material absorbs photons that the *p*-material could not absorb. One notices that the highest attainable efficiency does not rise. Summarized, when both materials absorb light, the highest maximum attainable efficiency reached is the same as in the case where only one material absorbs light, but higher efficiencies are reached for materials which have not optimal energy levels.

4 CONCLUSIONS

A maximum efficiency of respectively 54.0 % and 53.3 % is reached for a stacked and monolithic organic tandem cell, taking into account a LUMO-difference of 0.2 eV between donor and acceptor, necessary for exciton dissociation. This maximum occurs for the stacked and monolithic tandem cell respectively at a configuration (E_{g1}, E_{g2}) of (1.7 eV, 0.9 eV) and (1.6 eV , 0.9 eV). The requirements for an almost optimal configuration for the stacked tandem cell are quite broad, permitting that the values of the bandgaps for optimal cells are not that strict. This is not the case for the monolithic configuration; especially the value of the bandgap E_{g1} of the first subcell is more critical than for a stacked cell. This means that for the production of tandem cells, the choice of good bandgap combinations (and thus material combinations) is much more limiting for a monolithic configuration as for a stacked configuration. When both donor and acceptor of each subcell absorb light, the highest maximum attainable efficiency reached is the same as in the case where only one material absorbs light. However, higher efficiencies are reached for materials which have not optimal energy levels.

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