

Modeling of nanostructured photovoltaics: the network model and the effective medium model

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Abstract Organic photovoltaic solar cells are promising candidates for solar energy conversion. They have the potential for cost effectiveness and mechanical flexibility. An organic bulk heterojunction solar cell consist of a nanoporous interpenetrating network of an n -type and a p -type (semi)conductor sandwiched between two electrodes with different work functions. The complicated 3-dimensional geometry of those cells is unmanageable with standard modeling. We have suggested two methods to model the I - V curves of those nanostructured solar cells: the network model in which the solar cell is represented by resistors and diodes, and the effective medium model in which the whole p - n nanostructure is represented by one single effective semiconductor layer. These models were compared and it was shown for example that in both models the structure, when illuminating the n -side, is tolerant to resistance in the n -network but not to resistance in the p -network.

Keywords: modeling, nanostructured solar cells, network model, effective medium

I. THE NETWORK MODEL

In the network model (NM), we decouple the effects at microscopic (nm) and macroscopic (μm) scale.

At a microscopic scale, the complicated 3-dimensional nanoporous geometry of two interpenetrating networks is simplified to a quasi-periodical nanoscale ordering of an n - and a p -type (semi)conductor, forming a “unit cell”. It has been recognised before that nanoscale unit cells are almost field free. The periodical boundary conditions in a nanoscale periodic structure even lower the field for the same unit cell size [1,2]. It is called a “flat-band cell”: the total band bending can be totally neglected; the conduction and valence band are flat, as well as both Fermi levels (or electrochemical potentials) E_{Fn} and E_{Fp} .

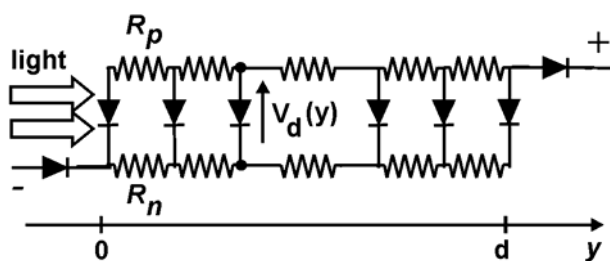


Fig. 1: A one-dimensional network connection of the unit cells, represented by the diodes, used to simulate the macroscopic cell. The resistors stand for the percolation of the p -network (top), and the n -network (bottom). Two contact diodes describe possible Schottky barriers at the electrodes.

At a macroscopic scale, we simplify the two interpenetrating networks to an electrical network. In a real solid-state nanostructured solar cell, a 3-dimensional n -type network makes electrical contact with one electrode. The p -

type network forms a complementary network which makes contact to the opposite electrode. To keep the model manageable, both networks are simplified to one dimension. We obtain the network shown in Fig. 1. Each diode in the row stands for a periodic, flat-band unit cell as just described. The resistors stand for the percolation in the p -network (top), and in the n -network (bottom). Two contact diodes describe possible Schottky barriers at the electrodes.

II. THE EFFECTIVE MEDIUM MODEL

In the effective medium model (EMM), the whole p - n nanostructure is represented by one single effective medium semiconductor layer. We consider selective contacts, i.e. one contact only accepts electrons, the other one only accepts holes. This creates the driving force for the separation of generated electron-hole pairs. The effective medium is characterized by an “averaging” of the properties of the n - and the p -material. The effective medium has one conduction band namely the conduction band of the n -type material or the lowest unoccupied molecular orbital (LUMO) of the acceptor molecule in a bulk heterojunction solar cell. The effective medium has also one valence band namely the valence band of the p -type material or the highest occupied molecular orbital (HOMO) of the donor molecule in a bulk heterojunction solar cell. This configuration is then fed into a standard solar cell device simulator, e.g. SCAPS [3]. Also other carrier related properties of the effective medium semiconductor are given by the corresponding material: the mobility μ_n , the diffusion constant D_n , the effective density of states N_C of the conduction band are those of the n -material, whilst the values of μ_p , D_p , N_V are those of the p -material. Non-carrier related properties, such as the dielectric constant ϵ , the refractive index n , and the absorption constant α are influenced by both materials. The precise way in which this happens depends strongly on the details and the size scale of the intermixing.

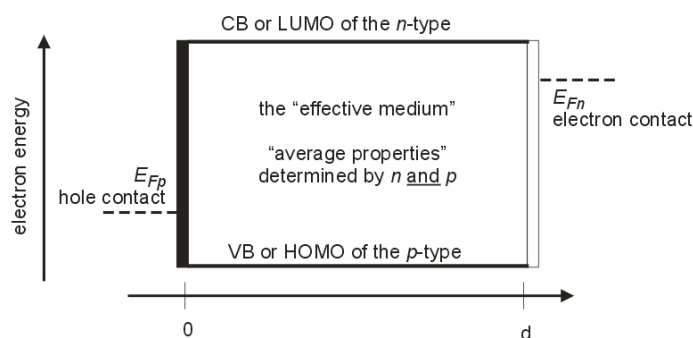


Fig. 2: Schematics of the effective medium model. The intimate blend of an n -type material and a p -type material is represented by one single ‘effective’ material with ‘average’ properties.

III. RESULTS OF SIMULATIONS

In our previous articles [1, 2], it was shown that in a simplified NM, i.e. constant resistances R_p and R_n , the solar cell performance is tolerant to R_n upon illumination on the n -side (electron selective contact). This resistance R_n of the n -type network can even be beneficial to the open circuit voltage V_{oc} and to the solar cell efficiency if the absorption α is high enough. On the other hand, even a small resistance R_p of the p -type network deteriorates the cell efficiency rapidly. This can be understood as follows: the cells are illuminated from one side, which implies that the unit cells generate less current and voltage as the light penetrates in the cell. Ideally, all generated currents are added to obtain the total light current. The open circuit voltages however are not summed, they are rather averaged. This is an essential difference with classical solar cells. Under illumination, the unit cells at the illuminated side are below their own local $V_{oc}(y)$ because all cells in the stack of Fig. 1 are forced to be at the same voltage. For the same reason, the cells in the bulk and at the rear end of the stack are above their local $V_{oc}(y)$. In Fig. 3 we see that a non-zero resistance in the n -sub-network improves the cell efficiency η if the resistance is not too high [4]. This is because cells deep in the stack, adversely contributing to V_{oc} , are effectively decoupled by a larger R_n . The voltage $V_d(y)$ over the elementary cells is now non-uniform, the cells at the illuminated side carrying a larger $V_d(y)$. This is favorable for the open circuit voltage of the whole cell, which equals $V_{oc} = V_d(0)$ when $R_p = 0 \Omega$ (see Fig. 1); the cells at the front are able to carry their generated hole current with no losses to the rear contact. This is also the reason why resistance in the p -sub-network is detrimental: it decouples the most illuminated cells at the front from the rear contact. Fig. 3 shows that a value of $R_n A = 150 \Omega \text{cm}^2$ is beneficial and $R_n A = 500 \Omega \text{cm}^2$ can be tolerated, whereas a value of $R_p A$ exceeding $1 \Omega \text{cm}^2$ is detrimental.

The question arises if the EMM gives similar results. Therefore, simulations with SCAPS were done using the EMM [4]. Again, the cell is illuminated from the n -side (the electron selective contact). Instead of the resistance of the NM, the parameter in the simulations of the EMM is the mobility μ of the carriers. Simulations were done with the electron and hole mobilities varying from $10^{-4} \text{cm}^2/\text{Vs}$ to $10^2 \text{cm}^2/\text{Vs}$.

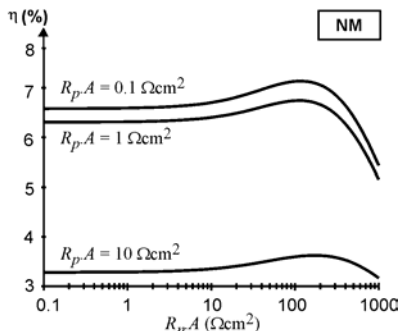


Fig. 3: Solar cell efficiency η as a function of the resistance $R_n A$ in the n -sub-network calculated with the NM. The parameter is the resistance $R_p A$ in the p -sub-network. Calculated with $\alpha = 10^5 \text{cm}^{-1}$. Note the sensitivity of η to $R_p A$.

The results in Fig. 4 show that for the EMM the relative efficiency η only deteriorates for low electron mobilities μ_n and that a low hole mobility μ_p is very detrimental (corresponding with high resistances R in the NM). Notice the similarity with Fig. 3 of the NM. It is remarkable that both

results correspond, because the NM was calculated for constant values of R_n and R_p , whilst in the EMM the resistivity and the mobility can vary over up to 7 orders of magnitude.

More detailed studies show that, if the absorption is high enough, the cell efficiency even rises for low electron mobilities thanks to an improved open circuit voltage V_{oc} ; the cell efficiency does not suffer from a lower electron mobility μ_n unless it is below 10^{-3} à $10^{-4} \text{cm}^2/\text{Vs}$, depending on the absorption α . This result is similar to the NM where a rise in the resistance R_n of the n -network also improved cell efficiency thanks to a better V_{oc} .

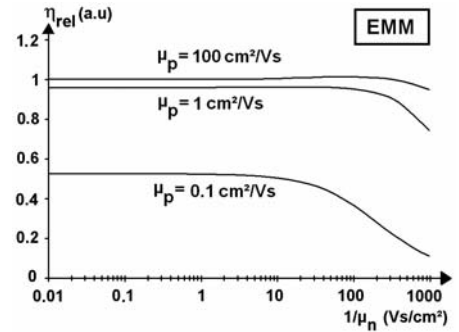


Fig. 4: Relative solar cell efficiency η as a function of the inverse electron mobility $1/\mu_n$ calculated with the EMM. The parameter is the hole mobility μ_p . Calculated with $\alpha = 10^5 \text{cm}^{-1}$.

Simulations with the hole mobility μ_p as parameter show that the short current density J_{sc} quickly drops when the hole mobility is lower than approximately 1 à $0.1 \text{cm}^2/\text{Vs}$. This is the reason for the deterioration of the cell when the hole mobility is too low. Again, this result is similar to the NM where a small resistance R_p of the p -network drops the cell efficiency rapidly. Because both models are symmetrically set up, the role of the p and n sub-network will be interchanged when we illuminate the cell from the p -contact side.

IV. CONCLUSIONS

We have suggested two methods to model the I - V curves of nanostructured solar cells: the NM and the EMM. In both models the structure, when illuminating the n -side, is tolerant to resistance in the n -network but not to resistance in the p -network. This could be an explanation for the substantially poorer behavior of “dry” or all solid-state cells compared to “wet” or dye sensitized solar cells [5]: the ion conduction in the electrolyte is better than the hole conduction in the solid-state p -conductor, and this is crucial for the cell performance, as we showed. Resistance in the n -network is not crucial, it is even beneficial if not too large.

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