The band-gap enhanced photovoltaic structure

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View online: http://dx.doi.org/10.1063/1.4948383
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The band-gap enhanced photovoltaic structure

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(Received 28 February 2016; accepted 19 April 2016; published online 2 May 2016)

We critically examine the recently suggested structure that was postulated to potentially add 50% to the photo-conversion efficiency of organic solar cells. We find that the structure could be realized using stepwise increase in the gap as long as the steps are not above 0.1 eV. We also show that the charge extraction is not compromised due to an interplay between the contact’s space charge and the energy level modification, which result in a flat energy band at the extracting contact. Published by AIP Publishing.

Thin film solar cells are attractive for the beyond-silicon applications, and often, the active region is not within a P-N junction. In the field of organic solar cells, it is known that the loss of open circuit voltage, relative to the absorption gap, is very high. This is mainly evident in the ultimate efficiency being well above reported values and/or in the fact that an empirical loss of ca. 0.5 eV (Refs. 6–9) needs to be introduced. This gap between the actual and theoretical values is often attributed to the active materials where new ones have led to a reduced loss. In relatively recent publications, it was shown that the built-in potential is limiting the open circuit voltage in bulk heterojunction solar cells. This has led to a suggestion of an irregular device structure that may overcome this limitation. In this paper, we explore the properties of the suggested structure by simulating several device structures (see Figure 1).

In Figure 1, we show schematically the device structures to be studied in this paper. The full line depicts the standard device structure where the effective HOMO (valence) and LUMO (conduction) levels are uniform throughout the device. The dashed line represents the enhanced structure suggested in Ref. 12 where the LUMO (HOMO) level is raised (lowered) close to the electron (hole) extracting contact. As a fully continuous slope is difficult to fabricate, the insets show three stepwise structures to be studied as well.

For the analysis, we use the drift-diffusion-Poisson model reported in Refs. 12–14. Following Ref. 12, the bulk heterojunction is represented as an effective medium consisting of a semiconductor with a suitable gap. The effective bandgap is taken to be 1.36 eV, and the recombination is assumed to be only Shockley-Reed-Hall (SRH) type. For the density at which the traps are full, we use the value of \( 2n_i \cosh(\Delta E_T/2kT) = 10^{15} \text{cm}^{-3} \) with \( \Delta E_T \) being the trap position relative to the middle of the gap and \( n_i \) being the intrinsic charge density (i.e., due to the thermal excitation in the dark). The traps capture rate, which is the capture cross section times the trap density \( (C \times N_T) \), is taken to be relatively low as \( C_nN_T = 3.3 \times 10^3 \text{s}^{-1} \), and the trap release rate is set accordingly to ensure thermal equilibrium between the traps and the relative band (see supporting information of Ref. 13). We also assume 1 Sun illumination following an exponential type absorption, having absorption depth of 150 nm and a total of 40% being converted into free carriers.

As stated above, we include only SRH type recombination, which is known to be a monomolecular rate at high charge densities. On the other hand, it is known that most organic solar cell devices exhibit density dependent recombination which is often fitted to a power of 2 (i.e., bimolecular). As reported in Ref. 13, we found that if one employs a device model, with the electrodes being introduced in a self-consistent manner, the device response exhibits a bimolecular type loss even when no such loss is explicitly included in the model. Moreover, the experimental data were reproduced using SRH type recombination only and adding a bimolecular loss mechanism would only exaggerate the losses.

The physical explanation found, through the simulations, was that at high intensities some space charge is inevitably formed, thus bending the band a bit such that the charge extraction rate is reduced. A reduced extraction is balanced by an enhanced the recombination rate. As the extraction of both carriers is reduced, the signature is of a bimolecular loss. For the calculation of the J-V curves, the potential difference between the electrodes is being set and the simulations solves for the current density (both in dark and under 1 Sun). By scanning the potential difference, the full J-V is

![Graph showing J-V curves](image)

FIG. 1. Schematic description of the effective energy level (HOMO and LUMO) structure of the devices considered. Full line is the standard device structure. Dashed line is the enhanced structure where the bandgap is continuously increased across 30 nm towards the electrodes. The insets show three realizations of this increase, left to right, 3 steps of 0.1 eV, 2 steps of 0.15 eV, and one step of 0.3 eV.
found, and from it, the open circuit voltage is deduced \( (I = 0, V = V_{\text{OC}}) \).

In Figure 2, we show the simulated energy band diagram of four devices. We use the idealised structure, with fully continuous slope, and the maximum changes in the energy levels are zero for the standard device (Figure 2(a)), 0.1 eV (Figure 2(b)), 0.2 eV (Figure 2(c)), and 0.3 eV (Figure 2(d)). The black rectangles symbolize the contacts which are 0.2 eV into the gap with respect to the band edge at the interface. The dashed lines are the quasi Fermi levels which, as expected, are aligned with the contacts work-functions. Figure 2(a) shows that the effect of the space charge near the electrode interface is very small for the standard device. This is because we assume that the barrier height at the interface cannot be smaller than 0.2 eV, due to Fermi level pinning at surface states. Namely, the pinning on both sides results in a 0.4 eV loss of built-in potential relative to the electronic bandgap. Though small, we note that the shape of the band created by the space charge is opposite to that of the proposed enhanced structure (see Figure 1). The exact shape of the bands depends on the space charge distribution which, in turn, depends on the shape of the density of states (DOS) through the values of the generalized Einstein relation. Due to the complexity of the DOS at the electrode interface and the fact that we do not explicitly include the pinning effect, we ignore it in this publication and use a classical Einstein relation.

Figure 2(b) shows the band diagram for the enhanced structure having a 0.1 eV increase in the bandgap, at the electrode. We note that, close to the extracting electrode, the band-structure and space-charge effects seem to cancel each other, and the bands are practically flat. See the LUMO (HOMO) next to the electron (hole) extracting electrode. The gradient reaching 0.1 eV is reflected in the open circuit voltage, which was found to increase from 0.83 V to 0.92 V.

Figures 2(c) and 2(d) show that as the band-gap enhancement, at the interface, is increased to 0.2 eV and to 0.3 eV, a barrier for charge extraction starts to form. Surprisingly, for the 0.3 eV enhancement, the barrier for extraction is only about 3 kT which in practice is not a barrier at all (see also inset of Figure 2(d)). Nevertheless, the open circuit voltage \( V_{\text{OC}} \) increases only marginally from 0.98 V for the 0.2 eV enhancement to 1.03 eV for the 0.3 eV one.

To show the reason for this negligible enhancement of \( V_{\text{OC}} \), we present in Figure 3 the charge density distribution of electrons (full line) and holes (dashed line) for the four structures in Figure 2 at open circuit and under 1 Sun. At the bulk of the device, the electron and hole densities are equal and they depart only close to the contacts interface, giving rise to the space charge bending of the levels (see discussion above). We note that the change in charge density is most significant once the 0.1 eV enhancement is introduced and

FIG. 2. Simulated energy level diagram and quasi Fermi levels at open circuit voltage and under 1 Sun. The black squares denote the position of the electrodes. (a) The standard device structure. With enhanced bandgap at the electrodes of 0.1 eV (b), 0.2 eV (c), and 0.3 eV (d). The inset to (d) is a zoom on the LUMO level close to the electron extracting electrode.

FIG. 3. Charge density distribution at open circuit voltage and under 1 Sun for the four devices presented also in Figure 2.
the effect decreases for larger enhancements (matching the trend in $V_{OC}$). The reason for this suppressed effect is that the recombination in the bulk is going up with the charge density, thus placing a limit on the maximum attainable density (or $V_{OC}$). In fact, the numbers presented in Figure 3 suggest that neglecting higher order recombination, as exciton-polaron,\cite{15,24} is probably not justified for the large enhancement case, at least for some of the materials used.\cite{22} We return to this point at the discussion.

The last aspect we examine is the use of a continuously changing band gap instead of a more realistic step wise increase. In fact, what we are after is the maximum allowed step height for the band shape to be considered effectively continuous. In Figure 4, we present calculated J-V curves under 1 Sun for the standard device (full line), the continuous enhancement to 0.3 eV (dashed), the 1 step of 0.3 eV (dashed-dotted), the 2 steps of 0.15 eV each (dotted), and the 3 steps of 0.1 eV each (long dashed-dotted), see the insets of Figure 1 for the schematic structures. We note that 0.1 eV steps can be regarded as very close to the ideal continuous change. As the figure shows, “small” covers up to about 0.1 eV and larger steps are no longer compensate for and the extraction barrier is becoming detrimental. Another interesting effect is exhibited by the 0.3 eV step device, showing that the barrier for extraction is accompanied by enhanced $V_{OC}$. From Figure 2, we note that when the extraction barrier is diminished, the band edge at the extracting electrode is at almost equal energy to the bulk of the device. As the contact is 0.2 eV below the band edge at the interface, the Fermi level in the bulk cannot exceed this 0.2 eV difference. The existence of extraction barrier implies that the band edge at the extracting interface is raised with respect to the bulk thus allowing the charge density (and Fermi level) to be a bit higher with respect to the no extraction barrier case. We refer to this effect as a reduced contact induced recombination.

To conclude, we have critically studied the enhanced structure suggested in Ref. 12. We found that the interplay between the electrode space charge and the energy level structure is what allows for effective charge extraction even when the gap is enhanced by 0.3 eV. This implies that the existence of space charge is essential or, in other words, that the contact still needs to be very good (ohmic) for the full potential to be realized. The materials used to enhance the effective bandgap need to be chosen carefully with the band gap discontinuity being kept below 0.1 eV (Figure 4). We found that 10 nm long step work well, but this needs to be taken as a starting point only due to potential practical effects such as interface mixing. Interestingly, the PCE curve for the single 0.3 eV step shows that the open circuit voltage is still limited by contact recombination, but with the current approach, one cannot recover it fully without compromising the charge extraction capabilities. Figure 3 shows that the 50% enhancement in photoconversion efficiency (PCE) suggested in Ref. 12 will require bulk heterojunction morphologies that suppress exciton-polaron annihilation\cite{15} and other high order losses. For current structures, it would be more reasonable to expect 25% to 30% enhancement only.

The research at Technion was partially supported by the Adelis Foundation for renewable energy research within the framework of the Grand Technion Energy Program (GTEP) and by the Ollendorff Minerva center.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Simulated current density–voltage characteristics of devices having continuous energy level increase to 0.3 eV (dashed, blue), the 1 step of 0.3 eV (dashed-dotted, purple), the 2 steps of 0.15 eV each (dotted, black), and the 3 steps of 0.1 eV each (long dashed-dotted, green). The J-V for the standard structure is shown, for reference, as full line (red). See the insets to Figure 1 for the schematic structures.}
\end{figure}