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Carrier collection in optically resonant nanostructures for quantum dot solar cells

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One of the most interesting - but often underappreciated - absorber materials for solar cells are PbS quantum dot (QD) layers. In principle, the tuneable bandgap, that derives from quantum confinement, together with strong absorption, which allows for thin and flexible layers, as well as the ease of fabrication in form of solution deposition, are each strong arguments for thin-film-QD absorber layer based solar cells. However, so far, those advantages have been met with notable disadvantages which have hindered a faster and more enthusiastic uptake of QD absorber layers in the scientific community. A major hindrance is the low diffusion length of charge carriers in the absorber, limiting the maximum possible absorber thickness, thus requiring an unsatisfying compromise between short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}). In this work, we lay out a path on how to address this issue, by introducing a 3-dimensionally structured p-n heterojunction (Fig.1) that can increase charge carrier generation, as well as improve extraction in comparison to flat cell geometries.

The structure in Figure 1 was derived from optical simulations (Lumerical FDTD), by maximizing the absorption per unit volume in the QD-layer. This is done by structuring the interface between the n-type ZnO and the p-type PbS QD layers such that the PbS-QD cylinders that are formed interact resonantly with light. Figure 2 shows a comparison between a flat cell and a cell with an optimized pattern, using the same absorber volume. It becomes clear that the absorption is enhanced across almost the full spectrum, increasing towards larger wavelengths, and mainly benefiting from two distinct mechanisms. Firstly, a Fabry-Perot resonance is shifted towards the high energy tail of the first exciton peak of the quantum dots, around 800 nm, and therefore addresses the weak absorption that usually occurs in this range. This gain in absorption is due to the QD-pillar's large optical cross-section, that channels light, that would otherwise propagate through the surrounding ZnO, into the pillars. Moreover, the periodicity of the structure allows it to sustain certain quasi-guided modes, which occur as narrow peaks in the absorption spectrum, around 750, 900 and 950 nm. The placement of the two modes at 900 and 950nm at the low energy tail of the exciton peak allows for a much sharper absorption onset.

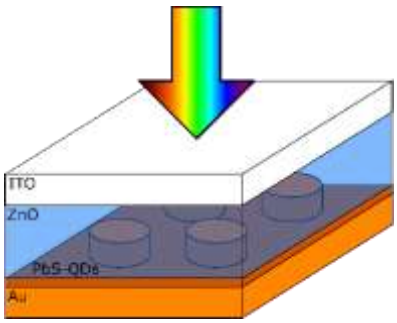

Figure 1: Schematic representation of the patterned PbS-QD solar cell geometry. Light is incident from the top. The cylindrical, optical QD resonators sit on a thin residual layer of QDs.

Thus far, we have outlined conventional design and quantification of light trapping, which basically follows the idea of maximizing J_{SC}. However, depleted-hetero junction solar cells, like this QD solar cell, strongly rely on the built-in electric field that spans across the junction interface into the absorber. Furthermore, the carrier diffusion length is comparable to the feature size of the patterned junction and as a result, charge extraction will also be significantly influenced by this optically optimized geometry[1,2]. This becomes clear when looking at the charge carrier generation profile (Figure 3), which corresponds to the spatially resolved absorption across the absorber layer,

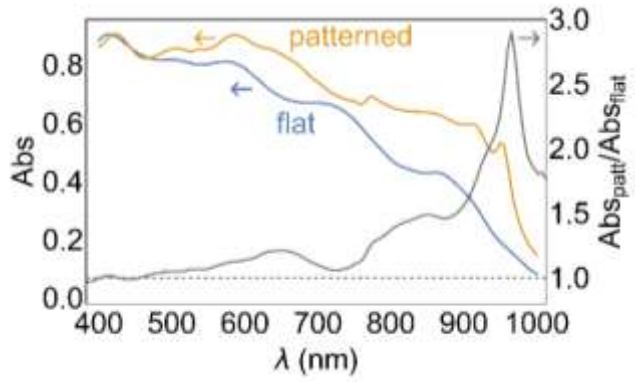

Figure 2: Comparison of simulated absorption of a flat (blue) and a patterned (yellow) PbS QD solar cell using the same absorber volume, corresponding to a thickness of 180 nm for the flat cell. The relative absorption enhancement is shown in grey. The dashed, grey line corresponds to a relative absorption enhancement of 1.

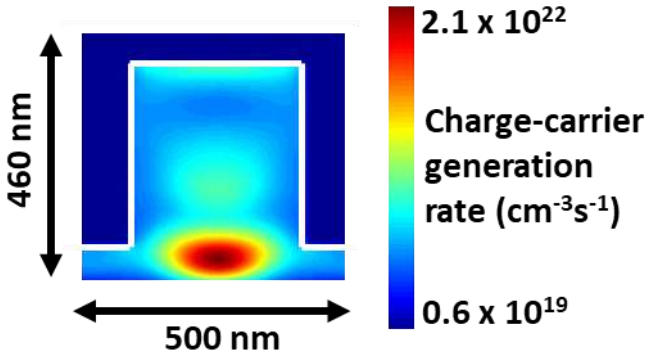

Figure 3: Charge-carrier generation profile across the p-n junction. The white line represents the interface between the ZnO and QD layers. Light is incident from the top. Negligible generation occurs in the ZnO layer (dark blue region). Most of the generation occurs close to the rear of the junction (red region).

weighted by the solar spectrum. Instead of a Beer-Lambert-law-like attenuation of the generated carrier density across the absorber layer, the structure causes the bulk of the generation to happen close to the rear of the solar cell. This is especially interesting when one considers the average distance that each charge carrier is required to travel to reach its respective extraction interface. In the case of an electron, the ZnO interface is on average much closer than in the case of a flat cell. In the case of a hole, most of them are generated much closer to the rear of the cell, where a thin (30nm) p+-type QD-layer acts as a hole selective interface. Furthermore, the shift of the bulk of the generated charge carriers towards the rear of the cells also favours extraction of holes, which in general have lower mobilities than electrons in QD-layers. Effectively, this benefits the V_{OC} as the non-radiative recombination loss is reduced[3]. Furthermore, the V_{OC} of such a cell benefits in a second way, namely from higher carrier generation per unit volume. This increases the quasi-fermi level splitting, similarly to the concentration effects in concentrator solar cell geometries[3].

The simulated JV-curves (Lumerical CHARGE) in Figure 4 illustrate a comparison between 3 distinct cells. The optically optimized cell with the structured heterojunction, a reference cell that uses the same absorber volume (180nm), as well as one that uses the same pn-junction thickness (400nm). The patterned cell seems to combine the generated J_{SC} of a thick absorber layer, along with the V_{OC} of a thin cell, avoiding an unsatisfying compromise. However, due to a low fill factor (FF), the patterned cell does not outperform the thin cell but shows a similar efficiency. At the moment, this is subject to further investigation, but one likely possibility is recombination losses related to holes that are generated far away from the rear of the cell, along with slower charge extraction due to weak electric fields in that region.

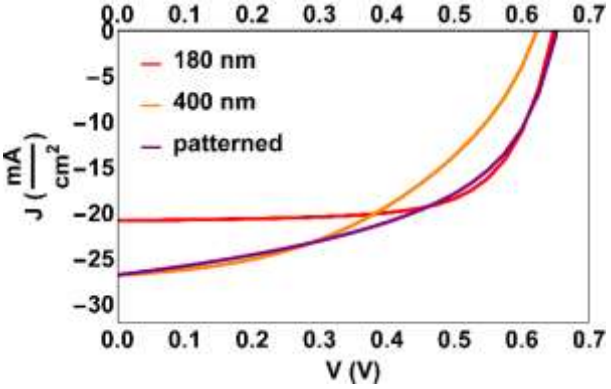

Figure 4: Comparison of JV-curves for three distinct cells. A flat cell with 180 nm absorber thickness (red), a flat cell with 400 nm absorber thickness (orange), and a patterned cell (purple) with a volume corresponding to 180 nm effective absorber thickness, but an actual height that corresponds to a 400 nm thick absorber layer.

The structure is currently being fabricated, with the intention of obtaining an ITO - patterned ZnO - QD absorber - Au geometry. To pattern the ZnO interface, we employ an imprint technique that derives from substrate conformal soft-imprint lithography (SCIL[4]). However, instead of using the associated silica solgel as a mask for a etch/lift-off sequence, we directly pattern the ZnO layer with a PDMS stamp (Figure 5a). This simple, one step patterning approach ensures that the electronic properties of the ZnO layers stay comparable to ZnO in flat cell geometries. Subsequent filling of the holes in the structure with QDs (Figure 5b), as well as Au-evaporation, finalises the cell fabrication.

Overall, we introduce a design that optimises absorption in the QD layer, and we investigate the expected electronic properties. Our results suggest that there is an opto-electronic optimum to be found and we will also outline how a coupled optimization between solvers for Maxwell's equations (Lumerical FDTD) and the Drift-Diffusion-Equations (Lumerical CHARGE) can yield high efficiency cell designs. Furthermore, we will show results on the experimental performance of such cells and compare them with our simulations.

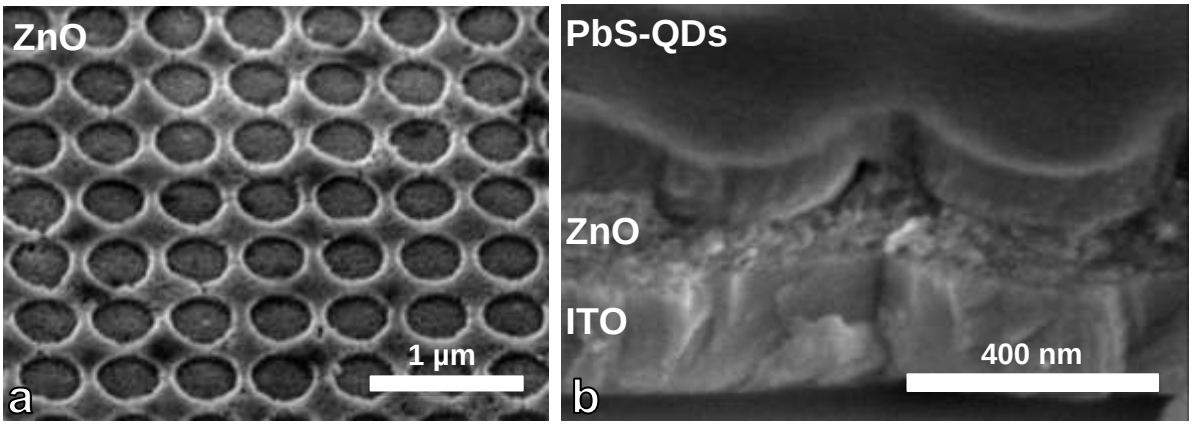

Figure 5: Image of a directly patterned ZnO-layer on an ITO substrate (a). Cross-sectional SEM image of a patterned structure, illustrating the alignment of the QD-layer in the holes provided by the ZnO layer (b). The structure here is inverted compared to Figure 1.

References

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