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Device physics of colloidal quantum dot solar cells

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Speirs, M. J. (2017). *Device physics of colloidal quantum dot solar cells*. University of Groningen.

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Summary

The need for clean, sustainable sources of energy, and the abundance of solar power incident on the Earth's surface, has driven the research in photovoltaics both in industry and academia. Currently, highly crystalline materials such as silicon dominate the photovoltaic market. Module efficiencies of commercial silicon solar cells reach 16-18%, while efficiencies in the lab are as high as 25%, which approaches the Shockley-Queisser limit of 33% for single junction solar cells. However, the production of highly pure silicon involves high manufacturing costs, resulting in both a long monetary and energetic payback time. Therefore, a cheaper method of producing solar cells is desirable. Solution processable semiconductors are a viable alternative approach, and much progress has been made using organic, and more recently, hybrid perovskite semiconductors. However amongst other challenges, the absorption of these materials is limited to wavelengths below 1 μm , and long term stability against oxygen and water still remains an issue.

Instead, colloidal lead sulfide quantum dots (PbS QDs) can potentially combine low cost production methods with high efficiency and good air stability. Due to their quantum confined nature, the bandgap can be controlled by varying the QD diameter, allowing the absorption onset to be tuned throughout the near infrared. In addition, the possibility of efficient multiple excitation generation could potentially allow PbS QDs to overcome the Shockley-Queisser limit. Finally, the large surface to volume ratio inherent to this material means that the electronic properties can be controlled via chemical control of the nanocrystal surface. Initially, the nanocrystals are covered by long aliphatic molecules which allow solubility in non-polar solvents. These ligands are electrically insulating however, and must be replaced by shorter molecules to bring the QDs in electronic contact with each other. A wide library of molecules is available with which not only the charge carrier mo-

bility can be altered, but also the energy levels with respect to the vacuum level, and even the Fermi level. At the same time, the ligand exchange process often introduces detrimental trap states and effective passivation of these traps is still a matter of much interest.

In this thesis we investigate several strategies for improving solar cell performance, both by altering the device structure and by changing the chemical nature of the QD surface.

In Chapter 2, we focus on efficient absorption of the solar spectrum using tandem solar cells featuring both inorganic and organic semiconductors as subcells. First, we fabricate a device using PbS QDs as the front subcell and a bulk-heterojunction of the polymer poly(3-hexylthiophene) (P3HT) and the fullerene [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as the rear subcell. We connect the subcells with a new interlayer comprising 1 nm aluminium and 5 nm tungsten oxide, with which we get an open circuit voltage (V_{OC}) equal to 92% of the sum of the subcells, indicating that the interlayer is able to effectively act as a recombination centre for electrons from the PbS QD layer and holes from the organic layer. We then perform simulations of the light distribution in tandem devices where the relatively wide-bandgap P3HT is replaced by a small bandgap polymer as rear subcell, and do the same for devices where the order of subcells is reversed. Device structures with a small bandgap polymer as the front subcell and PbS QDs as the rear subcell are the most promising, able to reach a short circuit current (J_{SC}) of 12 mA/cm².

In Chapter 3 we investigate a new strategy for passivating traps on the PbS nanocrystal surface. Instead of focusing on a post deposition treatment of the film, we incorporate a thin (~0.1 nm) passivating shell of CdS on the nanocrystal surface during the synthesis, which forms a type-I heterojunction with PbS. Simple Schottky junction solar cells are used to compare properties of the PbS and PbS-CdS films. Devices with the core-shell quantum dots display a significantly higher V_{OC} than solar cells with the core only QDs. We show that this effect is not due to an increased bandgap, nor due to a shifted Fermi level, but that it is due to lower trap density, reducing the pinning of the quasi Fermi levels under illumination. We then fabricate field effect transistors (FETs) with both core-shell and core only QDs. In the n-type channel, the passivation effect is evidenced by an increased gating effect in the output curves, and as a decrease in the sub-threshold swing in the transfer characteristics. Both phenomena can be explained by a reduced Fermi level pinning

to the trap states. This effect is not seen in the p-type channel, indicating that mostly electron traps near the conduction band are passivated by the CdS shell.

In Chapter 4 some of the limiting factors of state of the art inverted solar cells are probed using temperature dependent measurements. The active layer consists of a layer of n-type PbS capped with tetrabutylammonium iodide (TBAI) and a layer of PbS capped with ethanedithiol, which is either n-type or p-type depending on its level of oxydation. The active layer is sandwiched between TiO_2 and MoO_3 which function as hole and electron blocking layers, respectively. The solar cells display an impressive power conversion efficiency (*PCE*) of up to 9.4% at room temperature. When the device is cooled down, a significant increase in *PCE* is observed up to 240 K, due to an increasing V_{OC} and fill factor (*FF*), while the J_{SC} remains approximately constant. The V_{OC} increases due to a decrease of the reverse saturation current, which is found to follow the p-n junction model. The charge carrier mobility, measured using single carrier devices, is found to decrease with lower temperatures, leading to a smaller diffusion length. In light of the constant J_{SC} , this means that these devices are not limited by charge carrier diffusion, and the transport must be dominated instead by drift. This is confirmed by calculations of the depletion region, which extends almost throughout the device at room temperature. At lower temperatures, the depletion region increases, which improves the band-bending and facilitates charge extraction. In addition, the distribution of the depletion region across the p-n junction is found to undergo a beneficial shift towards the n-type PbS layer which, due to the higher charge carrier mobility, causes an increase in *FF*. Based on these findings at low temperature, we predict that increasing the doping concentration of the p-type layer to at least one order of magnitude higher than the n-type layer will increase the overall device efficiency at room temperature.

This prediction is put to the test in Chapter 5. We explore a new method of doping via post-deposition exposure of EDT-capped PbS to sodium hydrosulfide (NaHS). Increasing the ratio of sulfur on the PbS surface shifts the Fermi level towards the valence band and leads to more p-type QDs. Solar cells with the same structure as in Chapter 4 are made with undoped EDT-capped layers and with layers of EDT which have been treated with a solution of NaHS in methanol. The doped solar cells exhibit a higher J_{SC} and *FF* than the undoped references, leading to an absolute efficiency enhancement of 0.5%. Schottky diodes are then used to explore the reason for this. Equal charge

carrier lifetimes and ideality factors are found, indicating that the recombination mechanisms are not affected by the doping process. Instead, a decreasing J_{SC} in the Schottky solar cells indicates a decreasing depletion region, which can be caused by an increased doping concentration. This is confirmed by Mott-Schottky analysis, with which a threefold increase of the doping concentration is found in the films treated with NaHS. An even higher doping concentration is expected to further improve the solar cell efficiency.