Article type: Full Paper

Title Optimization of charge carrier extraction in colloidal quantum dots short-wave infrared photodiodes through optical engineering

Epimitheas Georgitzikis*, Pawel E. Malinowski, Jorick Maes, Afshin Hadipour, Zeger Hens, Paul Heremans and David Cheyns

E. Georgitzikis, Prof. P. Heremans
imec vzw; Kapeldreef 75, 3001, Heverlee, Belgium
KU Leuven, Kasteelpark Arenberg 10, 3001, Heverlee, Belgium
E-mail: Epimitheas.Georgitzikis@imec.be

Dr. P. E. Malinowski, Dr. David Cheyns, Dr. Afshin Hadipour,
imec vzw; Kapeldreef 75, 3001, Heverlee, Belgium

J. Maes, Prof. Z. Hens
Physics and Chemistry of Nanostructures, Ghent University, Krijgslaan 281-S3, 9000, Ghent, Belgium
Center for Nano- and Biophotonics (NB-Photonics), Ghent University, 9000, Ghent, Belgium

Keywords: photodetectors, quantum dots, infrared light, carrier transport, optical modeling

Colloidal quantum dots (QDs) have attracted scientific interest for infrared optoelectronic devices due to their bandgap tunability and ease of fabrication on arbitrary substrates. In this work, we demonstrate short wave infrared photodetectors based on lead sulfide (PbS) QDs with high detectivity and low dark current. Using a combination of time-resolved photoluminescence, carrier transport and capacitance-voltage measurements, we prove that the charge carrier diffusion length in the QD layer is negligible, such that only photogenerated charges in the space charge region can be collected. To maximize the carrier extraction, we develop an optical model for PbS QD based photodiodes and through optical engineering we optimize the cavity at the wavelength of our choice. This universal optimization recipe is applied to detectors sensitive to wavelengths above 1.4 μm , leading to external quantum efficiency (EQE) of 30% and specific detectivity (D^*) in the range of 10^{12} Jones.

1. Introduction

Imaging in the infrared (IR) wavelength range is essential for many applications such as low-light / night vision, surveillance, sorting, biometrics and medical diagnostics.^[1] As silicon cannot be used to detect wavelengths above 1000 nm, imagers designed for the short-wave infrared (SWIR) range are based on semiconductors with a smaller bandgap, such as InGaAs and HgCdTe, combined with a Si-based CMOS readout circuit in a so-called hybrid imager.^[2] These materials have been thoroughly investigated over the last years leading to high performance detectors. However, such hybrid solution sets a fundamental limitation to the smallest pixel size that can be achieved and leads to very expensive detectors. In that respect, colloidal quantum dots (QDs) are a very interesting material group for the fabrication of infrared imagers due to their unique opto-electronic properties. Quantum confinement allows the tuning of the nanocrystal bandgap according to their size, enabling detection at different wavelengths of the infrared spectrum, while their electrical properties depend on the proper selection of ligands.^[3] Additionally, the fact that they can be dispersed in solution and deposited over a large area makes them great candidates for low cost sensors, since they can be facilely integrated on top of the readout circuit enabling monolithic infrared imagers.^[4–6]

A lot of scientific effort has been devoted in the last years to improving the performance of QD photodiodes by the use of more efficient ligand passivation techniques^[7–9] or the device stack optimization^[10,11] leading to very high external quantum efficiencies (EQE) in a broad wavelength spectrum (up to 1 μm). However, for imaging applications, additional figures of merit such as the signal to noise ratio, the detector response speed and the detectivity in a specific and narrow wavelength range must be maximized. Recent studies demonstrated that larger diameter QDs are characterized by lower absorption coefficients making it harder to achieve high EQE values further in the IR region.^[12,13] In the state of the

art, two types of PbS-based detectors are dominant for the short-wave infrared wavelength region, namely photoconductors^[14,15] and photodiodes^[16–18]. Photoconductors rely on amplification gain and suffer from low response speed which makes them inappropriate for megahertz imaging. Schottky diodes have led to high QE and fast SWIR detectors but the high dark current is a limiting factor towards the realization of an actual imager. Photodiodes using n-p junctions have been studied and applied in solar cells^[19] and photodetectors^[20]. These devices can combine a low dark current and fast response.

In this work, we analyze the limits of the charge carrier extraction in colloidal quantum dot photodetectors, and we apply this understanding, in conjunction with optimization of the optical performance, to maximize the efficiency of photodetectors at the wavelength of 1.4 micron. The charge carrier extraction mechanisms of narrow bandgap QD films are analyzed by time-resolved photoluminescence, carrier transport and capacitance-voltage measurements, enabling the determination of the carrier density, lifetime and mobility. From the calculated short diffusion length of the minority carriers, we deduce the need to achieve a wide depletion region to minimize recombination and thus enhance the carrier harvesting. Subsequently, these data are used as feedback into process optimization of photodiodes based on an n-p heterojunction architecture, in which the junction is formed by a QD photoactive film and a metal oxide that acts as an n-type electron transport layer (ETL). Using optical modeling based on a transfer matrix method, we optimize the thickness of the transport layers to maximize the intrinsic cavity effect of the device structure at the wavelength that matches the IR absorption peak of the QDs, taking the limited depletion width into account. The result is a considerable boost in the QD layer absorption leading to high quantum efficiencies in the SWIR. In the fabricated devices, this boost is combined with a low dark current ($\sim \mu\text{A}/\text{cm}^2$), leading to specific detectivity in the range of 10^{12} Jones.

2. Results and Discussions

We selected lead sulfide QDs with a diameter of 5.5 nm (see experimental section and Figure S1, Supporting Information) synthesized by hot-injection method.^[21] Here, the use of substituted thioureas enables the production of gram scale batches in a reproducible way. The NIR photoactive layer with a peak wavelength absorption at 1440 nm, is sandwiched between two transparent transport layers with good conductivity, and hence tunable thickness (see Figure 1a for the layer stack structure). The photodiode junction is created at the interface between the niobium-doped titanium dioxide layer ($\text{TiO}_2\text{:Nb}$)^[22] and the PbS QDs capped with 1,4-Benzenedithiol (1,4 BDT)^[23,24]. Transmission Electron Microscope (TEM) inspection of the layer-by-layer grown QD material revealed perfect crystallinity within the QDs, high level of super-crystallinity within a single layer and random orientation between layers. Figure 1b depicts a schematic band diagram of the junction formed between the wide band-gap $\text{TiO}_2\text{:Nb}$ and the PbS QDs, using energy level values from literature.^[25–29] The carriers that are photo-generated inside the space charge region will drift by the built-in potential to the respective electrode while carriers that are generated in the quasi-neutral region must diffuse towards the space charge region in order to be collected. In the next sections, we present an in-depth analysis of the drift and diffusion mechanisms describing the transport of the photo-generated carriers and we quantitatively assess their limitations.

The electrical field in the space charge region of the photodiode causes carriers to drift towards the contacts. For a p-n junction, this space-charge region originates from the carrier depletion from one side of the junction towards the layer with an opposite majority carrier profile. Assuming that the carrier concentration of the $\text{TiO}_2\text{:Nb}$ is much higher than the one of the QDs we can consider a one sided junction.^[26,27] The depletion width (W) of such a one-sided junction is:

$$W = \sqrt{\frac{2 \varepsilon_r \varepsilon_0 (V_{bi} - V)}{q N_{QD}}} \quad (1)$$

where ε_r is the effective-medium dielectric constant of the QD layer, ε_0 is the vacuum permittivity, V_{bi} the build-in potential, q the elementary charge and N_{QD} the doping concentration of the QD film.^[30] In order to obtain ε_r and N_{QD} , capacitance-voltage (C-V) measurements are performed on Schottky diodes with a structure of ITO/PbS/Al. Assumingly fully depleted devices (QD thickness 50 - 75 nm) are used to obtain the dielectric constant from the parallel plate capacitor model $C = (A\varepsilon_r\varepsilon_0)/d$, where A is the diode surface area and d is the PbS layer thickness. As shown in Figure 2a, the measured capacitance remains constant in the range of 10^2 to 10^5 Hz and for biases between -0.5 V to 0 V, confirming that the diode is fully depleted. The dielectric constant can be accurately obtained at 14 ± 1 , a value that matches the results presented in literature through theoretical models.^[31]

To determine the doping concentration, a Schottky diode structure with a thick (~250 nm) and thus not fully depleted PbS QD layer is processed. Using the Mott-Schottky equation,^[11]

$$\frac{1}{C^2} = \frac{2 (V_{bi} - V)}{q \varepsilon_r \varepsilon_0 N_{QD}} \quad (2)$$

the N_{QD} is obtained from the slope of $1/C^2$ versus the applied bias and found to be in the range of 2.3×10^{17} and 3.1×10^{17} (Figure 2b). Then the carrier density and the determined dielectric constant are applied in Equation 1, in order to calculate the depletion width in the p-n junction devices, which is found to be around 65 ± 10 nm at 0 V bias, while at 2 V reverse bias it increases to 135 ± 10 nm. These values are also confirmed by performing C-V measurements on the p-n junction photodiodes and the voltage-dependent depletion width can be determined directly from $W = \varepsilon_r \varepsilon_0 / C(V)$ (Figure S2, Supporting Information).

Charges photo-generated outside of the space charge region are required to diffuse across the quasi-neutral region to be collected by the respective electrode. The distance that

the carriers can travel before they recombine is defined by their diffusion length which can be calculated as

$$L = \sqrt{D \tau} \quad (3)$$

where τ is the carrier lifetime and D the diffusion coefficient, linked to the charge carrier mobility μ via the Einstein –Smoluchowski relation $D = \frac{kT}{q} \mu$ (with k the Boltzmann's constant, and T the temperature).

The carrier lifetime in the QD film is obtained using time resolved photoluminescence (TRPL) on glass / PbS layers. The PL decay as a function of time,^[32] (Figure 3a), corresponds to the decay of the minority carriers. From these data, we retrieve a minority carrier lifetime of only 15 ns.

To determine the carrier mobility in the PbS film, single carrier devices exhibiting space charge limited current (SCLC) are fabricated using an ITO/QD/Ag structure for electron-only devices and ITO/PEDOT:PSS/QD/MoO_x/Au for hole-only devices. Figure 3b shows a current density-voltage curve (J - V) and the results of the fitting obtained using the SCLC mechanism in a hole-only device. The results for an electron-only device are shown in Figure S3. At low bias voltages (< 0.1 V), the device follows an Ohmic behavior with J being proportional to V . As the bias increases, the injected carriers start to dominate, filling trap states of the film and the current density becomes proportional to the square of the applied voltage ($J \sim V^2$). When all of the traps are filled, there is an exponential current increase, followed by another region with a $J \sim V^2$ behavior following the Mott-Gurney law,^[33]

$$J_{MG} = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{d^3} \quad (4)$$

where d is the active layer thickness. From the Mott-Gurney region of the J - V curves, we extracted the mobility of holes and electrons in the range of $4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

Knowing the lifetime and mobility, the diffusion length of the minority carriers can be readily calculated from Equation 3 and is found to be extremely short - less than 1 nm. This result indicates that there is a limitation on the distance that the carriers can travel before they recombine; thus carrier extraction based on diffusion can be excluded. We conclude that for maximum photocurrent, we cannot rely on carrier diffusion, but rather, fully depleted devices should be considered.

Taking into consideration the preceding analysis, we determine that the maximum usable QD layer thickness in our photodiode structure falls in the range of the depletion width (maximum 150 nm). Achieving high efficiencies with only a few hundred nanometers is a big challenge due to the low capture cross-section for short-wave infrared light (extinction coefficient below 10^4 cm^{-1}). However, an advantage of using thin layers that are in the range of the incident light wavelength is the possibility to create a standing light wave inside the photodiode stack. Reflection and transmission of the light takes place at interface between two materials due to the difference of their refractive indices. Furthermore, contact metals act as mirrors reflecting all the light back to the photodiode stack. As a result, positive and negative interference takes place, creating points of high and low light intensities. A proper optical design of the devices can shift the highest light intensity to the place where an exciton dissociation center is located, while at the same time minimize losses. This can lead to a significant enhancement of the detector quantum efficiency.

The characteristic optical properties of the materials used, required for the modeling are incorporated into the complex index of refraction $\underline{n} = n + ik$ where n is the refractive index and k the extinction coefficient. Thin layers of QD material are deposited on Si / SiO₂

substrates, and measured using variable angle spectroscopic ellipsometry. The data can be fitted using a dispersion law consisting of a Cauchy dependence and Lorentzian absorption peaks for the complex index of refraction. However, due to the low extinction coefficient of the PbS QD films, the ellipsometry data obtained are not sufficient for accurate modeling. In the next phase, values with improved accuracy are obtained by fitting the transmission and reflection data (R/T) of QD layers on glass. The R/T of three different thicknesses are fitted simultaneously using transfer matrix modeling, starting from the dispersion law as obtained from ellipsometry. Using this approach, the data as shown in Figure 4 are obtained. The complex index of refraction for the other materials in the photodiode stack is directly obtained from ellipsometry.

The optical constants are subsequently used as an input for a transfer matrix method, adapted to our device structure, simulating the behavior of the light as it impinges on the photodiode.^[34,35] As shown in Figure 4c, the used layers are stacked between a semi-infinite transparent glass substrate and a semi-infinite ambient atmosphere. The light falls into the multilayer from the left, through the glass substrate and for each layer can be resolved in two separate terms: a component propagating in the positive (E^+ , moving in the same direction as the incident light) and one in the negative direction (E^-). Using the thickness d_i of each layer and its complex index of refraction $\bar{n}_i$, obtained above the electrical film of each component can be calculated and subsequently the total electrical field inside our devices as plotted below for the wavelength of interest (1440 nm). The expected absorption for the device stack can be retrieved, as well as the expected absorption of each individual layer and the expected photodetector external quantum efficiency (EQE) at the target wavelength. The developed model comes in full agreement with the experimental data (Figure S4, Supporting Information). Additionally, the thickness of each layer can be optimized to obtain the highest possible EQE values.

First, we simulate the effect of the QD layer thickness on the performance of the device, with fixed thicknesses for the transport layers. In order to incorporate the drift-limited optical active zone in the stack, we split the simulated QD film into two layers: one resembling the depleted layer close to the $\text{TiO}_2\text{:Nb}$ that will contribute to the photocurrent generation, and one resembling the photocurrent inactive part, in which the generated carriers will recombine. The simulation is performed by sweeping the total QD film thickness and the depletion width. The expected EQE at the wavelength of 1440 nm (Figure 5a) demonstrates that for a depletion width in the range of 130 nm, a local maximum of 25% can be reached for a QD film of around 150 nm, while a depletion width larger than 350 nm is required to achieve EQE values above 40%. To check the validity of the simulations, photodiodes are fabricated with selected QD layer thicknesses in the range of 45 nm to 300 nm and transport layer thicknesses at 5 nm and 20 nm for the HTL and the ETL respectively. The trend between measured EQE values, the depletion width and the total QD thickness (Figure 5b) follows the results predicted by the simulations. Furthermore, the devices with an active layer of 120 ± 10 nm show the highest EQE values, hence, this is the QD layer thickness that can lead to the most efficient photon-to-carrier conversion and should be used for further optimization.

Notwithstanding the optimization of the QD layer thickness, further enhancing of the optical cavity can be achieved by fine tuning the other layers in the photodiode stack. Using again optical simulations with a fixed QD layer thickness to the previously found optimum of 120 nm, we analyze the optical losses in the stack and we efficiently minimize them at the target wavelength of 1440 nm. The analysis of optical losses in the layer stack used above is shown in Figure 6. It is clear that ITO is the main responsible for these losses, since it is characterized by a high absorption in the infrared spectrum, above 40% at the spectral area of 1.4 μm (Figure S4, Supporting Information). To minimize this absorption, simulations are performed by sweeping the $\text{TiO}_2\text{:Nb}$ and the HTL thicknesses and monitoring the expected

EQE and ITO absorption (see Figure 6a and Figure 6b). A proper selection of the transport layer thicknesses will improve the detector EQE notably, while the ITO absorption is minimized. These observed trends are subsequently used as a feedback towards the optimization of the actual devices. The analysis of the optical losses shows indeed a steep decrease in the light lost due to ITO absorption in the target spectrum after the fine tuning of the transport layers. The result is the fabrication of photodiode detectors with enhanced absorption at the wavelength of 1440 nm demonstrating an EQE value higher than 30% as shown in Figure 7a. Additionally, these optimized devices are characterized by a dark current lower than $1 \mu\text{A}/\text{cm}^2$ (Figure 7b) at 2 V reverse bias, leading to a peak in the specific detectivity at the target wavelength with a value of $\sim 7 \times 10^{11}$ Jones, which is one of the highest reported values for PbS QD photodiode detectors in this range of the IR spectrum.

3. Conclusion

In this work, we describe a methodology for the enhancement of the photo-generated carrier harvesting in PbS QD photodiode detectors for infrared light absorption, and use the methodology to optimize a SWIR photodiode. This methodology is based on a combination of thorough analysis of the dominating carrier extraction mechanisms, with optical engineering of the photodiode stack. The aforementioned techniques are applied on photodiodes formed by a heterojunction of a metal oxide ($\text{TiO}_2\text{:Nb}$) and an infrared sensitive PbS QD film. Due to the demonstrated short diffusion length, we deduce the need to fabricate fully depleted devices, setting a maximum thickness of 150 nm to the QD layer. For these fully depleted devices, further improvement of the detector performance is realized through an optical design. Using transfer matrix simulations, we maximize the intrinsic cavity effect of the device structure and enhance the EQE of our photodiodes at 1440 nm, reaching values of $\sim 30\%$. Finally, we can conclude that improving the diode junction by increasing the depletion

width in the examined system, as well as improving the carrier diffusion length within the QD film, may further improve the quantum efficiency.

4. Experimental Section

QD synthesis: Lead oleate was synthesized from lead trifluoroacetate according to a previously described method.^[21] Also, N-4-MeO-phenyl-N'-dodecylthiourea was synthesized according to Hendricks et al. Lead oleate (10.281 g, 13.35 mmol, 1.5 equiv) and n-dodecane (150 mL) are added to a 250 mL 3-neck round bottom flask equipped with a stirring bar and coupled to a Schlenk line. The set-up is stirred for 1h under N₂ flow at 120 °C. In a nitrogen-filled glovebox, N-4-MeO-phenyl-N'-dodecylthiourea (3.0 g, 8.89 mmol) and 1-methoxy-2-(2-methoxyethoxy)ethane (5 mL) are mixed in a 10 mL vial. The vial is sealed with a rubber septum and taken outside. Both vessels are then heated to 135 °C and once the temperature is stable, the solution of thiourea is quickly injected into the clear colorless lead oleate solution via a syringe. The reaction is allowed to run for 5 minutes at 135 °C before the flask is cooled with a water bath. Once cooled to room temperature, toluene (60 mL) is added and the resulting slurry is split between centrifuge tubes and centrifuged (2000 RCF, 10 minutes). The dark nanocrystal dispersion is decanted and any remaining solids are discarded. Acetone (150 mL) is then added to precipitate the nanocrystals. After centrifugation (2000 RCF, 5 minutes), the clear, pale brown solution is discarded and the remaining nanocrystal residue is redispersed in toluene. Five more cycle of precipitation from toluene with acetone are performed to reach a ligand coverage of 4.1 oleate ligands per square nanometer as measured by ¹H NMR spectroscopy. Finally, the resulting 1.8 g of 5.5 nm sized PbS QDs are dispersed in n-octane and stored in an nitrogen-filled glovebox.^[36]

Device Fabrication: The photodiodes are fabricated using a solution-based process except of the top metal contact that is thermally evaporated. TiO₂:Nb dispersion in ethanol^[37] is spin coated on glass substrates with pre-patterned ITO lines cleaned previously in a deep of

soap, water, acetone and IPA. Subsequently, the PbS QD film is deposited in air by spin-coating a 15 mg/ml solution of PbS QDs in octane. Once dried, 1,4-BDT dissolved in acetonitrile is applied to the substrate for 30 seconds and spun dry. Then the substrate is washed with acetonitrile. The thickness of the QD film can be increased by repeating the deposition cycles multiple times. Then the Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (PolyTPD) is spin-coated. The stack is completed with the thermal evaporation of 100 nm of silver (Ag). The device area is defined by the overlap of the top and bottom electrodes at 0.13 cm². For the Schottky diodes the QD layers are directly deposited on the glass/ITO substrates, while the Schottky junction is formed with the evaporation of 100 nm thick Aluminium (Al). For the single-carrier devices, poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS; VP AI4083, H. C. Stark) is used as a HTL, spin-coated at 2500 rpm from water and annealed at 120 °C for 10 min in order to achieve a 50 nm thick film. Additionally, the 5 nm thick molybdenum oxide (MoO_x) used is thermally evaporated.

CV measurements: Capacitance voltage measurements of the diodes are performed using a Keysight E4980A Precision LCR Meter, superimposing 10 mV of AC bias over the DC bias and at frequency range between 20 Hz to 1 MHz.

Photoluminescence measurements: PbS QD films are deposited on quartz substrates using the layer-by-layer technique mentioned above. The PL measurements are performed using a Hamamatsu PL lifetime spectrometer. The QD film is excited by a 532 nm laser and the photoluminescence is measured in wavelengths ranging from 380 nm up to 1650 nm.

EQE and R/T measurements: Spectral response measurements are performed using a Bentham PV300 Spectral Response system. A light beam from a Xenon/Quartz halogen source is coupled into a Bentham TMc300 single monochromator, giving a coverage over the spectral range of 300-2500nm. The reflection and transmission measurements are executed using an integration sphere.

Current-Voltage characterization: IV sweeps are carried out in N₂ environment using a Keithley 2400 source-meter.

Ellipsometry: Optical constants and film thickness of the materials are measured using a variable angle spectroscopic ellipsometer (Semilab, ges5)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The results reported in this paper have been realized with the funding of Agentschap Innoveren & Ondernemen (VLAIO) in the framework of project MIRIS (IWT/150029).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] M. Pilling, P. Gardner, *Chem. Soc. Rev.* **2016**, 45, 1935.
- [2] J. Jiang, S. Tsao, T. O'Sullivan, M. Razeghi, G. J. Brown, *Infrared Phys. Technol.* **2004**, 45, 143.
- [3] P. R. Brown, D. Kim, R. R. Lunt, N. Zhao, M. G. Bawendi, J. C. Grossman, V. Bulovic, *ACS Nano* **2014**, 8, 5863.
- [4] A. Rogalski, *Prog. Quantum Electron.* **2003**, 27, 59.
- [5] P. E. Malinowski, E. Georgitzikis, J. Maes, I. Vamvaka, F. Frazzica, J. Van Olmen, P. De Moor, P. Heremans, Z. Hens, D. Cheyns, *Sensors* **2017**, 17, 2867.
- [6] T. Rauch, M. Böberl, S. F. Tedde, J. Fürst, M. V. Kovalenko, G. Hesser, U. Lemmer, W. Heiss, O. Hayden, *Nat. Photonics* **2009**, 3, 332.
- [7] J. Tang, K. W. Kemp, S. Hoogland, K. S. Jeong, H. Liu, L. Levina, M. Furukawa, X. Wang, R. Debnath, D. Cha, K. W. Chou, A. Fischer, A. Amassian, J. B. Asbury, E. H. Sargent, *Nat. Mater.* **2011**, 10, 765.

- [8] Z. Zhang, Z. Chen, L. Yuan, W. Chen, J. Yang, B. Wang, X. Wen, J. Zhang, L. Hu, J. A. Stride, G. J. Conibeer, R. J. Patterson, S. Huang, *Adv. Mater.* **2017**, 1703214, 1703214.
- [9] X. Lan, O. Voznyy, A. Kiani, F. P. García de Arquer, A. S. Abbas, G.-H. Kim, M. Liu, Z. Yang, G. Walters, J. Xu, M. Yuan, Z. Ning, F. Fan, P. Kanjanaboos, I. Kramer, D. Zhitomirsky, P. Lee, A. Perelgut, S. Hoogland, E. H. Sargent, *Adv. Mater.* **2016**, 28, 299.
- [10] R. Saran, R. J. Curry, *Nat. Photonics* **2016**, 10, 81.
- [11] H. Yu, S. Liu, S. Baek, D. Y. Kim, C. Dong, F. So, *J. Mater. Chem. C* **2016**, 4, 11205.
- [12] I. Moreels, K. Lambert, D. Smeets, D. De Muynck, T. Nollet, J. C. Martins, F. Vanhaecke, A. Vantomme, C. Delerue, G. Allan, Z. Hens, *ACS Nano* **2009**, 3, 3023.
- [13] Z. Hens, I. Moreels, *J. Mater. Chem.* **2012**, 22, 10406.
- [14] C. Hu, A. Gassenq, Y. Justo, K. Devloo-Casier, H. Chen, C. Detavernier, Z. Hens, G. Roelkens, *Appl. Phys. Lett.* **2014**, 105.
- [15] A. De Iacovo, C. Venettacci, L. Colace, L. Scopa, S. Foglia, *Sci. Rep.* **2016**, 6, 37913.
- [16] E. Heves, Y. Gurbuz, *Procedia Eng.* **2012**, 47, 1426.
- [17] E. Heves, C. Ozturk, V. Ozturk, Y. Gurbuz, *IEEE Electron Device Lett.* **2013**, 34, 662.
- [18] J. P. Clifford, G. Konstantatos, K. W. Johnston, S. Hoogland, L. Levina, E. H. Sargent, *Nat. Nanotechnol.* **2009**, 4, 40.
- [19] M. Yuan, M. Liu, E. H. Sargent, *Nat. Energy* **2016**, 1, 16016.
- [20] B. N. Pal, I. Robel, A. Mohite, R. Laocharoensuk, D. J. Werder, V. I. Klimov, *Adv. Funct. Mater.* **2012**, 22, 1741.
- [21] M. P. Hendricks, M. P. Campos, G. T. Cleveland, I. Jen-La Plante, J. S. Owen, *Science* **2015**, 348, 1226.
- [22] A. Hadipour, WO2017108710A1.pdf **2017**.
- [23] D.-K. Ko, A. Maurano, S. K. Suh, D. Kim, G. W. Hwang, J. C. Grossman, V. Bulović,

- M. G. Bawendi, *ACS Nano* **2016**, *10*, 3382.
- [24] J. Tang, L. Brzozowski, D. A. R. Barkhouse, X. Wang, R. Debnath, R. Wolowiec, E. Palmiano, L. Levina, A. G. Pattantyus-Abraham, D. Jamakosmanovic, E. H. Sargent, *ACS Nano* **2010**, *4*, 869.
- [25] T. Salim, Z. Yin, S. Sun, X. Huang, H. Zhang, Y. M. Lam, *ACS Appl. Mater. Interfaces* **2011**, *3*, 1063.
- [26] A. Trenczek-Zajac, Mieczyslaw Rekas, *Mater. Sci.* **2006**, *24*, 1.
- [27] H. Wu, L. Wang, *J. Chem. Phys.* **1997**, *107*, 8221.
- [28] J. Wang, J. Polleux, J. Lim, B. Dunn, *J. Phys. Chem. C* **2007**, *111*, 14925.
- [29] B. R. Hyun, Y. W. Zhong, A. C. Bartnik, L. F. Sun, H. D. Abruna, F. W. Wise, J. D. Goodreau, J. R. Matthews, T. M. Leslie, N. F. Borrelli, *ACS Nano* **2008**, *2*, 2206.
- [30] S. M. Sze, K. K. Ng, *Phys. Semicond. Devices, 3rd Ed. John Wiley Sons, Inc.; NJ* **2007**, 164.
- [31] D. D. W. Grinolds, P. R. Brown, D. K. Harris, V. Bulovic, M. G. Bawendi, *Nano Lett.* **2015**, *15*, 21.
- [32] J. H. Warner, E. Thomsen, A. R. Watt, N. R. Heckenberg, H. Rubinsztein-Dunlop, *Nanotechnology* **2005**, *16*, 175.
- [33] J. Kwan Kim, J. H. Song, H. Choi, S. Jae Baik, S. Jeong, *J. Appl. Phys.* **2014**, *115*.
- [34] L. A. A. Pettersson, L. S. Roman, O. Inganäs, *J. Appl. Phys.* **1999**, *86*, 487.
- [35] H. Gommans, D. Cheyns, T. Aernouts, C. Girotto, J. Poortmans, P. Heremans, *Adv. Funct. Mater.* **2007**, *17*, 2653.
- [36] J. Maes, N. Castro, K. De Nolf, W. Walravens, B. Abécassis, Z. Hens, *Chem. Mater.* **2018**.
- [37] M. Niederberger, *Acc. Chem. Res.* **2007**, *40*, 793.

Figure 1. a) Photodiode stack architecture. The infrared photo-active layer is formed by a layer of PbS quantum dots. Transmission Electron Microscopy shows the superlattice formed by the QDs and reveals high level of crystallinity; b) Schematic band diagram at equilibrium showing the p-n junction formed between the doped TiO_2 and the PbS QD layer and the drift and diffusion mechanisms.

Figure 2. Capacitance-voltage measurements for Schottky diodes using a structure of ITO/QD/Al; a) Capacitance as a function of frequency at three bias conditions for a relatively thin PbS QD layer (~50 nm). b) Mott-Schottky plot for a thick, not fully depleted PbS QD layer.

Figure 3. a) Time resolved photoluminescence measurements lifetime spectra of 5.5 nm QDs capped with 1,4-BDT b) J-V plot of single carrier PbS QD photodiode demonstrating the Ohmic, trap filled and space charge limited current (SCLC) regions.

Figure 4. Complex index of refraction for measured using variable angle spectroscopic ellipsometry and reflection/transmission measurements. a) Fit of the reflection and transmission data for three different thicknesses of the QD film with the complex index of refraction model determined by ellipsometry. b) The final n and k values for the 5.5 nm QDs demonstrating a peak at about 1440 nm c) Multiple reflection and transmission in the examined multilayer stack, sandwiched between two semi-infinite ambient layers (glass substrate and air). Light is incident from the glass substrate. The electrical field in each layer has two components, propagating in the positive (E^+) and the negative (E^-) direction and together they form the total electrical field. The normalized modulus squared of the electrical field for the wavelength of 1440 nm is plotted.

Figure 5. Optical simulations a) monitoring the expected EQE at the wavelength of 1440 nm with variable QD layer thickness and depletion width and b) comparing the simulated values with the experimental results of fabricated photodiodes. The error bars indicate the uncertainty in the QD layer thickness (± 10 nm) and the variation in the EQE results obtained from measuring different diodes that have the same QD layer thickness.

Figure 6. Optimization of carrier harvesting at 1440 nm for a photodiode using a fully depleted 120 nm QD layer and analysis of the optical losses in the full stack. a) optical simulations for variable transport layer thicknesses in order to achieve the maximum possible EQE and b) the minimum possible loss in the ITO; c) before device optimization the optical loss in the ITO is 40% at 1440 nm, while d) after optimization using 30 nm and 90 nm of

HTL and ETL thickness respectively the loss in the ITO is reduced to 10% and the absorption of the QD layer is increased.

Figure 7. Performance characteristics of the optimized fabricated devices a) EQE and Detectivity b) current density under dark conditions.