Device physics of colloidal quantum dot solar cells
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This introductory chapter is devoted to the basic concepts relating to colloidal quantum dots. After introducing the main physical and chemical properties of quantum dots, a short history of their use in solar cells is given. The relevant physics and advantages of various solar cell structures is then discussed. Finally, an outline of this thesis is given.
Chapter 1. Introduction

1.1 Solar energy

In 1905, Albert Einstein published the four *Annus Mirabilis* papers which would revolutionize physics. The first of these publications explained the photoelectric effect,[1] i.e. the production of charge carriers upon absorption of light, by proposing that light comes in discrete packets of energy known as quanta. This discovery lay the foundation for modern day quantum physics and many technological breakthroughs, and lies at the heart of solar cell operation.

The development of solar cells is a response to the ever increasing need for energy linked to modern day life. The growing global population and the fast economic growth of some of the world’s most populous countries means that the demand for energy will grow significantly in the next couple of decades. Average global power consumption is expected to increase by 48% between 2012 and 2040, from 18 TW to 27 TW.[2] Currently, about 76% of the world’s energy is supplied by fossil fuel and projections show that this percentage will remain high until 2040. However, estimates of the fossil fuel reserves and and untapped resources are highly uncertain, and it has become clear that large scale burning of fossil fuels is an unsustainable way of meeting our long term energy needs. At the same time, the CO\(_2\) emissions released as a result are contributing to the greenhouse effect and accelerating climate change.[3] Recently, the Paris Agreement on was signed by 174 countries and the European Union, stating that action must be undertaken to cut CO\(_2\) emissions in order to alleviate the effects of climate change, and specifically to limit the average global temperature increase to less than 2 °C.[4] To achieve this, a total CO\(_2\) emissions allowance of 590-1,240 Gton CO\(_2\) from 2015 onwards has been proposed.[5] With the current emission rate at approximately 40 Gton/year, it is clear that a shift towards cleaner forms of energy is required if this ‘budget’ is not to be exceeded within the next few decades. For this reason, an increasing amount of effort from both the scientific community and industry has focused on developing new sources of clean renewable energy, such as wind, hydro, and solar power.

Solar energy is particularly interesting due to the abundance of energy available for harvest. To be precise, average solar insolation exceeds the global power consumption by a factor of approximately 5,000, making solar energy an obvious candidate for large scale energy production. The most direct method of converting light to electricity is through photovoltaics (PV).
Currently, a global PV capacity of 230 GW PV has been installed, making up only slightly more than 1% of the world’s energy supply. Nevertheless, solar energy has been identified as a key factor in cutting CO$_2$ emissions and the capacity of installed PV is growing rapidly.

To elucidate the potential of photovoltaic materials for energy conversion, the limiting detailed balance efficiency of a single junction solar cell with a bandgap $E_g$ was calculated by Schockley and Queisser in 1961, taking into account only the four fundamental loss processes; the spectral loss of photons with energy lower than the bandgap ($h\nu<E_g$), the thermal loss induced by photons with energy higher than the bandgap ($h\nu>E_g$), blackbody radiation, and radiative recombination. The trade-off between spectral and thermal losses results in an ideal bandgap of 1.3 eV for single junction devices measured under 1 sun intensity of the standard AM1.5 solar spectrum. With this bandgap at most 33% of solar energy can be converted into electricity. Currently, silicon (Si) is the most pervasive material in solar cell market. With a bandgap of 1.1 eV, it lies close to the ideal bandgap for single junction solar cells, and Si is one of the most abundant elements in the Earth’s crust, making it an attractive material for PV applications. Commercial modules typically reach an efficiency of 16-18%, while single devices can reach impressive efficiencies of ~25% in the laboratory. Taking into account practical losses such as front reflection, these solar cells are remarkably close to the Shockley-Queisser limit, allowing only incremental efficiency improvements from here on. However, producing Si wafers with sufficient crystal purity for solar cells is an energetically expensive process. Moreover, due to the relatively low absorption coefficient of Si, thick layers are required to absorb most of the sunlight. These factors inherently induce high manufacturing costs, resulting in long monetary and energetic energy payback times which form an obstacle to widespread use. For this reason, much effort is devoted not only to improving the efficiency, but also to reducing the cost of solar cell production.

1.2 Solution-processable photovoltaics

An alternative approach is to use materials which can be fabricated from a solution, allowing for high throughput deposition techniques such as blade-coating, spray coating, and flexographic printing. The scalability of this new generation of solar cells allows competition with traditional Si technology on
a price per watt basis, potentially even if the final efficiency is lower.\cite{9}

Semiconducting polymers and small organic molecules were the first solution-processable materials used in solar cells and have been under continuous investigation for the last two decades due to their chemical adaptability and the ease with which they can be solubilized. In addition, the high absorption coefficient of these materials means that only a few hundred nanometres are needed to fully absorb the accessible light. This contributes to the cost efficiency and also allows organic solar cells to be fabricated on flexible substrates, opening up a wide variety of new applications for which the rigidity of Si is impractical. Organic semiconductors are characterized by alternating single and double bonds, i.e. conjugation, leading to highly delocalized molecular orbitals which allow intramolecular charge transport. Polymers used in PV possess side chains which provide solubility, while the backbone is formed by long chains of conjugated monomers along which charge carriers, usually holes in particular, can travel with relative ease. Intermolecular transport however, requires charges to hop from one molecular chain to the next, which, together with the disorder in polymer-polymer stacking, limits the charge carrier mobility in these materials. In addition, due to the low dielectric constant (or permittivity) of these materials, photo-excitations do not form free charge carriers as they do in Si. Instead, electrostatically bound electron-hole pairs, or Frenkel excitons, are formed with binding energies roughly an order of magnitude larger than the thermal energy available at room temperature. This necessitates the use of a heterojunction composed of both donor and acceptor materials as the absorbing layer in order to facilitate charge separation and reduce recombination processes. The nanoscale morphology of the donor-acceptor blend is crucial to the performance of organic solar the system, requiring prolonged optimization for each material combination and complicating device fabrication and analysis. Furthermore, long term stability is problematic since most organic semiconductors are sensitive to oxidation and moisture, and the conjugated bonds are susceptible to photo-degradation in UV light. Finally, the absorption onset of the most efficient organic solar cells is still limited to wavelengths below 1 µm, leaving a large portion of the infrared spectrum unused. Despite these difficulties, efficiencies of organic solar cells have improved from 2.9% in 1995,\cite{10} to 11% today,\cite{8} and research in this field is still ongoing.

Other solution-processable PV materials include quantum dots, which are the topic of this thesis, and hybrid perovskites, which have shown a remark-
able rise in efficiency over the last several years, but which make use of toxic and water-soluble compounds and currently exhibit low device stability and a larger than ideal bandgap. In the next section, a thorough introduction to colloidal quantum dots will be given.

1.3 Lead sulfide quantum dots

Colloidal quantum dots (QDs) form a promising and versatile class of solution-processable semiconductors. Clusters of inorganic semiconducting materials in the order of several nanometres in diameter are surrounded by a shell of organic molecules which stabilize the QD and provide solubility in non-polar solvents. Colloidal QDs potentially offer the advantages of inorganic semiconductors, i.e. high charge carrier mobility and good stability, with the benefits of high absorption coefficient and solution-processability. At the same time, colloidal QDs offer a wide range of adaptability due on the one hand to the large library of surface modifying ligands which alter the electronic properties, and on the other hand the size dependent optical properties stemming from the quantum confinement effect; i.e. when carriers in the crystal lattice are confined by the boundary of the QD, the available energy levels are quantized (Figure 1.1a). In addition, the bandgap $E_g$ widens with decreasing QD radius $R$ according to

$$E_g(QD) \approx E_{g,0} + \frac{\hbar^2 \pi^2 (m_e + m_h)}{2R^2 m_em_h}$$

where $E_{g,0}$ is the bandgap of the bulk semiconductor, and $m_e$ and $m_h$ are the effective mass of the electron and hole, respectively.

Lead sulfide (PbS) QDs in particular have emerged as a leading material for the fabrication of QD solar cells, and have been used in such applications as infrared sensors, infrared photon sources, transistors, and solar cells. PbS exhibits a cubic rock-salt crystal structure (Figure 1.1b) with a lattice constant of 5.93 Å. The reason for the success of PbS is due firstly to the facile synthesis which allows the reproducible production of monodisperse, relatively defect free nanocrystals, shown for example in Figure 1.1d. Secondly, the large Bohr radius of 18 nm for excitons in PbS means that QDs of sizes lower than 10 nm fall into the extreme quantum confinement regime. As a result, the bandgap, and the resulting absorption spectrum, can be shifted at will with careful control of the QD size during
Figure 1.1. a) Schematic energy levels of bulk (left) and confined semiconductor (right) b) Faceted QD with rock salt crystal structure from different angles c) Absorption spectra of QDs of different sizes d) TEM images of PbS QDs, clearly showing the rock-salt crystal structure.

Finally, the possibility of multiple carrier generation (MEG) in PbS QDs gives the potential to overcome the Shockley-Queisser limit in a single junction solar cell; the energy of a hot exciton with $E > 2E_g$ can in principle excite a second electron from the valence to the conduction band through impact ionisation. In bulk semiconductors, this process is inefficient because it involves three particles, and must compete with Auger recombination and with phonon-mediated cooling of the electrons and holes to their band edges. In bulk systems, the abundance of energy states favours the rapid thermal decay of the hot exciton. In confined systems, however, the separation of energy levels can be greater than typical phonon energies, retarding the thermal relaxation process. At the same time, because the charge carriers are confined
1.3. Lead sulfide quantum dots

to a very small volume, Heisenberg’s uncertainty principle relaxes the conservation of momentum requirement between the three particles, resulting in a more efficient MEG process. Reports have already shown internal quantum efficiencies of 150% in confined systems,[27] and MEG could theoretically raise the Schockley-Queisser limit to 44%.[28]

Charge transport in QD films is only possible when the quantum dots are in close proximity to one another, such that the wave-functions of charge carriers overlap with neighbouring quantum dots. This coupling between the QDs can be approximately quantified by the binding energy $\beta$, which is proportional to the probability $\Gamma$ that charge carriers can tunnel to adjacent QDs.[29]

$$\beta = h\Gamma \propto \exp\left(-2\Delta x \sqrt{\frac{2m^*}{\hbar^2} \Delta E}\right)$$  \hspace{1cm} (1.2)

with $h$ the Planck’s constant, $m^*$ the effective mass of the charge carrier, and $\Delta x$ and $\Delta E$ the energy barrier width and height, respectively. The coupling thus depends heavily on the separation between two adjacent QDs, and therefore on the length of the capping ligands and on the permittivity of intermediate matrix, which affects the barrier height. As mentioned, the colloidal stability of QDs is given by organic ligands such as oleic acid (OA) or oleylamine. These long aliphatic ligands provide solubility in non-polar solvents and stabilize the nanocrystal surface, but simultaneously form a large barrier to charge transport. To use this material in electronic application, the aliphatic ligands must therefore be replaced with shorter molecules, such that the wave-function-overlap between adjacent QDs becomes appreciable.

The ligands not only affect the material mobility, but can also change the position of energy levels, including the Fermi level, depending on their chemical nature and dipole moment.[30] The Fermi level is also affected by the stoichiometry of the QD surface. Excess lead atoms on the surface lead to a higher the density of states near the conduction band, leading to n-type PbS QDs, while excess sulfur on the surface leads to more p-type behaviour.[31] Altogether, PbS QDs offer a large toolbox with which the optoelectronic properties can be controlled.
1.4 A short history of colloidal QD solar cells

Initially, colloidal quantum dots, in particular CdSe, were used as infrared (IR) sensitizing acceptor materials in organic solar cells. Efficient charge transfer in polymer-QDs blends was first demonstrated by Greenham et al. in 1996.\cite{32} By studying the photoluminescence quenching of the conjugated polymer poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) in a blend with 4 nm diameter CdS or 5 nm diameter CdSe QDs, it was observed that when the QDs are capped with long trioctylphosphine oxide ligands (TOPO), photoluminescence quenching only occurs when there is a significant overlap between the absorption spectrum of the QD and the photoluminescence spectrum of the polymer, as is the case for CdSe. This indicates that exciton transfer, and not charge transfer, is taking place via resonant Förster energy transfer. However, after removal of the long TOPO ligands with pyridine, quenching was found to be significantly enhanced in both CdS and CdSe, indicating direct charge transfer toward the QDs, driven by the higher electron affinity of the QD materials compared to the polymer. The authors demonstrated that not only can the electron be transferred from the polymer to the QD, but that excitons created in the QD can also be dissociated by hole transfer from the QD to the polymer. In most systems, this is most readily evidenced by the contribution to the photocurrent external quantum efficiency ($EQE$) for wavelengths at which only the QD absorbs.\cite{33}

Compared to cadmium-based chalcogenides, lead-based chalcogenides have a much smaller bandgap, allowing for better sensitisation in the infrared, and can in principle (as intrinsic semiconductors) function both as donor or acceptor depending on their size.

In 2004 and 2005, McDonald et al. first showed the use of PbS QDs capped with octylamine for IR sensitisation of MEH-PPV.\cite{12,34} In 2009, Szendrei et al. showed that, depending on the size,\cite{35} OA-capped PbS (PbS$_{\text{OA}}$) can function as an electron donor, demonstrating efficient electron transfer to fullerenes.\cite{14} Shortly after, Jarzab et al. showed that PbS$_{\text{OA}}$ can simultaneously function as donor and acceptor in a ternary blend with poly(3-hexylthiophene) (P3HT) and the fullerene derivative [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM).\cite{36} In this case, the capping ligand on the QD surface plays a paramount role in determining charge transfer rates. Both octylamine and OA create a significant barrier to charge transport. On the other hand, thiol ligands such as 1,4-benzenedithiol (BDT), 1,2-ethanedithiol
Figure 1.2. Chemical structure of several very common ligands. a) Oleic acid b) Octylamine c) Trioctylphosphine oxide d) Tetrabutylammonium iodide e) 1,4-benzenedithiol f) Ethane dithiol g) Mercaptopropionic acid.

(EDT) and 3-mercaptopropionic acid (MPA) result in much smaller barriers for charge carriers and the strong affinity of the thiol groups to uncovered Pb atoms on the nanocrystal surface results in very efficient replacement of the native ligands. At the same time, their bidentate nature allows for inter-QD cross-linking, forcing the QDs into close proximity with one another (Figure 1.3) which increases wave-function overlap and allows pinhole- and crack-free QD solids to be formed, see Figure 1.3.\cite{[37]} With the introduction of these ligands, QDs emerged as a viable stand-alone material in solar cells.\cite{[38]}

Between 2007 and 2010, solar cells using only these QD solids improved steadily from \~2-5\% using the simple Schottky structure,\cite{[21,39,40]} to 5-7\% by 2012 using at least one charge-blocking interlayer.\cite{[41–43]}

The nature of thiol-capped PbS QDs depends on the degree of air exposure, with increased oxide content increasing the p-type doping.\cite{[37,44]} For this reason, n-type thiol-capped QDs can only be made in completely inert environment and the stability of the ensuing devices is generally low as a consequence. In 2012, salts featuring electron rich halide anions, in particular iodide, emerged as an excellent method to achieve air stable n-type doping.\cite{[30,45,46]} With both n- and p-type PbS available, efficiencies of \~8\% were soon achieved,\cite{[23]} and most recently, certified values have exceeded 11\%.\cite{[47]}

These successes notwithstanding, several issues need to be addressed before PbS QD solar cells can become a viable technology. Current state of
the art devices have active layers of ~300 nm, while a thickness of ~1 µm is necessary to absorb all the light in the infrared.\(^{[48]}\) Higher mobilities and lower recombination rates are first necessary before such thick layers can be used effectively. Imperfections to the crystal surface either resulting from the synthesis or from the ligand exchange process can lead to energy levels within the bandgap. For instance, it was shown that a dangling Pb atom on the surface leads to shallow donor states beneath the conduction band, and that a dangling S atom leads to a shallow acceptor state above the valence band.\(^{[49]}\) If deep enough, these energy levels can form detrimental trap states or centers for radiative or non-radiative recombination. Due to the high surface to volume ratio inherent to nanocrystals, large trap densities are common in QD solids, and improved passivation techniques are still needed. Furthermore, the polydispersity of QD themselves causes energetic disorder which can affect device performance in the same way, though presently this effect is small compared to that of trap states.\(^{[50]}\) Finally, PbS solar cells will need to show a very robust life cycle stability to satisfy the legislative and public perception issues caused by the toxicity of lead.

1.5 Solar cell characterization

In this section, an introduction is given to the characterisation and basic measurement techniques of solar cells. The performance of a solar cell is determined by the behaviour of the current density, defined as the current normalized to the device area \(J = I/A\), in response to an applied bias \(V\). A typical current-voltage \((J-V)\) curve in the dark is shown in Figure 1.4a. Without illumination, a solar cell shows diode-like behaviour, with small current
in reverse (negative) bias (region 1). At small bias, the shape of the $J-V$ curve is dominated by the symmetric shunt current resulting from the finite shunt resistance (2). At larger bias, exponentially increasing current can be seen (3) until, finally, the current becomes limited by the series resistance (4). Under illumination, a photo generated current shifts the entire curve downwards and the curve enters the fourth quadrant. In this quadrant, the current flows against the applied bias and power can be extracted from the device. Three important points can be identified on the $J-V$ curve, see Figure 1.4b. At zero bias ($V = 0$), the short circuit current ($J_{SC}$) is found. Here, almost all the photogenerated current can be extracted from the device, but the power ($P = J \cdot V$) is zero. Analogously, the open circuit voltage ($V_{OC}$) is the voltage achieved if the circuit is broken ($J = 0$). This is the maximum voltage the solar cell can deliver, but here too the power is zero. The point where maximum power can be generated ($J_{MPP}, V_{MPP}$) is found somewhere in between, and the power generated at this point is used to calculate the power conversion efficiency ($PCE$) under solar illumination with a power density $P_{in}$,

$$PCE = \frac{J_{MPP} \cdot V_{MPP}}{P_{in}}$$  \hspace{1cm} (1.3a)

$$= \frac{J_{SC} \cdot V_{OC} \cdot FF}{P_{in}}$$  \hspace{1cm} (1.3b)

where for the latter equality we have defined the fill factor ($FF$) as the ratio of the maximum area that can fit under the $J-V$ curve in the fourth quadrant.

*Figure 1.4. Typical $J-V$ curves of a QD solar cell. a) In the dark on a linear (solid) and semilogarithmic scale (dashed). b) Under AM1.5G solar illumination featuring the figures of merit of a solar cell.*
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and the area defined by the product of the $V_{OC}$ and $J_{SC}$

$$FF = \frac{J_{MPP} \cdot V_{MPP}}{J_{SC} \cdot V_{OC}}$$

(1.4)

The fill factor is a measure of the shape of the $J-V$ curve. The more square the curve is in the fourth quadrant, the higher the $FF$. The FF is the most complex figure of merit, and is determined by the competition between charge extraction and recombination.$^{[51]}$ Thus, we see that the efficiency can be expressed as the product of three figures of merit, each of which gives valuable information about the functionality of the solar cell. For high efficiency, all three values should be optimized simultaneously, since complex inter-dependencies prevent the isolated optimisation of individual figures of merit.

To ensure comparable evaluations of solar cell performance worldwide, testing should take place at 25 °C under 1000 W/m$^2$ intensity of the standard AM1.5G solar spectrum. This is the spectrum of the sun at Earth’s surface after it has been filtered by 1.5 atmospheric volumes, including scattered light. In the laboratory environment, full intensity AM1.5G light is not readily available and testing takes place under a simulated solar spectrum using a Halogen lamp in combination with a quartz filter. The intensity is calibrated with a Si solar cell certified by the Fraunhofer Institute for Solar Energy Systems, which has a known current under 1 Sun illumination and spectral response. The simulated spectrum used for solar cell characterisation is similar but not equal to the solar spectrum, and this difference must be taken into account for accurate testing. The correction factor, or mismatch factor $M$, depends on the spectral response of the solar cell under investigation and the spectral response of the reference solar cell

$$M = \frac{\int E_R(\lambda)S_R(\lambda)\delta\lambda}{\int E_S(\lambda)S_R(\lambda)\delta\lambda} \cdot \frac{\int E_S(\lambda)S_T(\lambda)\delta\lambda}{\int E_R(\lambda)S_T(\lambda)\delta\lambda}$$

(1.5)

Here, $E_R$ is the AM1.5G solar spectrum, $E_S$ is the spectrum of the solar simulator, $S_R$ is the spectral response of the reference cell, $S_T$ is the spectral response of the device under investigation, and $\lambda$ is the photon wavelength. The value of interest is the denominator of the right term, representing the calculated current of the test device under AM1.5G illumination. For very broadly absorbing materials, such as Si, mismatch factors are typically very close to unity, while for non-Si materials mismatch factors of 1.1-1.4 can be obtained, making the mismatch factor a crucial element to take into account.
The spectral response of the test cell can be obtained by measuring the external quantum efficiency (EQE), also called the incident-photon-to-current efficiency (IPCE), which is the ratio of extracted electrons to the number of photons incident on the solar cell. Under monochromatic light, the current of the test cell is measured, from which the number of extracted electrons can be calculated. The light intensity is measured using calibrated silicon and germanium photodiodes, from which the number of incident photons can be obtained. The EQE is then calculated for each wavelength in the range 380 to 1400 nm by

\[ EQE(\lambda) = \frac{hc}{q\lambda} \frac{J(\lambda)}{P_{in}(\lambda)} \] (1.6)

with \( h \) Planck’s constant, \( q \) the elementary charge, \( c \) the speed of light, and \( P_{in} \) the incident monochromatic light intensity.

![Figure 1.5. Typical EQE spectrum of a QD solar cell, measured under short circuit conditions. The red line shows the calculated cumulative current found by integrating the product of the EQE and the solar spectrum.](image)

The spectral response is simply the current extracted per incident watt of light and can be easily calculated from the EQE spectrum

\[ S(\lambda) = \frac{J(\lambda)}{P_{in}(\lambda)} \] (1.7a)

\[ = \frac{e\lambda}{hc} \cdot EQE(\lambda) \] (1.7b)
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Due to the sensitivity of the photocurrent to the light intensity, and the complications resulting from the mismatch between the solar and lamp spectra, the EQE serves as an important validation of the J-V measurements. The short circuit current expected under AM1.5G illumination can be calculated from the EQE via

$$J_{CALC} = \int \frac{q \lambda}{h \nu} EQE(\lambda) P_{AM1.5}(\lambda) \delta \lambda$$  \hspace{1cm} (1.8)

and should be equal to the $J_{SC}$ obtained from the J-V measurements performed under the solar simulator (Figure 1.4b). The implicit assumption made here is that the photocurrent scales linearly with light intensity ($J \propto I^\alpha$, with $\alpha = 1$), since the intensity of the monochromatic light used in the EQE measurements is usually much lower than 1 Sun intensity used for the J-V measurements. If $\alpha$ is less than unity, then $J_{CALC}$ gives an overestimation of the $J_{SC}$ under 1 Sun intensity and a correction factor is needed.

$$J_{CALC} = \int EQE(\lambda) P_{AM1.5}(\lambda) \left( \frac{P_{AM1.5}(\lambda)}{P_{in}(\lambda)} \right)^{\alpha-1} \delta \lambda$$ \hspace{1cm} (1.9)

with $P_{AM1.5}$ the intensity of the AM1.5 solar spectrum. A typical EQE spectrum is shown in Figure 1.5 together with the cumulative current calculated from Equation 1.8.

The EQE does not differentiate between losses caused by recombination of photogenerated charges and losses caused by the transmission or reflection of photons. A quantity more physically informative of the processes inside the solar cell is the internal quantum efficiency (IQE), defined as the ratio of extracted electrons to the number of absorbed photons. The IQE can be calculated from the EQE taking into account the portion of photons lost to reflection and transmission. If the rear metallic electrode is thick enough, transmitted light can be safely neglected ($T = 0$) and the IQE is given by:

$$IQE_{tot}(\lambda) = \frac{EQE(\lambda)}{1 - R(\lambda)}$$ \hspace{1cm} (1.10)

where $R(\lambda)$ is the reflectance of the solar cell.

The IQE defined in this way still includes losses caused by parasitic absorption by the electrodes and interlayers. If instead the charge collection
efficiency of photogenerated charge carriers in the active layer (AL) is of inter-
est, the \( IQE \) can be defined as

\[
IQE_{AL}(\lambda) = \frac{EQE(\lambda)}{A_{AL}(\lambda)} = \frac{EQE(\lambda)}{1 - R(\lambda) - A_{parasistic}(\lambda)} \quad (1.11)
\]

where \( A_{AL} \) is the fraction of absorbed photons in the active layer and \( A_{parasistic} \) is the fraction of photons absorbed by the electrodes and interlayers. Both definitions of the \( IQE \) are used, sometimes without distinction, in the literature. Though less physically informative, the \( IQE_{tot} \) is more accessible experimentally, since it requires only the straightforward measurements of \( EQE \) and the reflection. For the \( IQE_{AL} \), \( A_{AL} \) must be optically modelled, which requires full knowledge of the refractive indices of each material.

Finally, the \( J_{SC} \) is given by

\[
J_{SC} = \int IQE_{AL}(\lambda)A_{AL}(\lambda)P_{AM1.5}(\lambda) \, \delta\lambda \quad (1.12)
\]

For high current, the product of \( IQE_{AL} \) and \( A_{PbS} \) should be as high as possible. Often, a trade-off exists between maximizing absorption using thick active layers on one hand, and on the other hand maintaining high \( IQE \), which decreases with increasing active layer thickness. For this reason careful optimisation of the active layer thickness is required for efficient solar cells.

### 1.6 Solar cell operation

In their most general form, solar cells comprise an active layer formed by one or more semiconducting absorbers sandwiched between two electrodes, possibly with electron or hole blocking layers in between. Upon photon absorption in the active layer, an electrostatically bound electron-hole pair (exciton) is formed by the excitation of an electron from the valence to the conduction band. If the binding energy of the exciton is sufficiently low, it can be dissociated into free charge carriers thermally or by the presence of an electric field. The binding energy depends on the permittivity of the material, and for PbS QDs, like for most inorganic materials, the permittivity is typically very high (~18-20 for PbS QDs) so the charge carriers are essentially free at room temperature.

For a semiconductor in the dark, the number of electrons occupying the conduction band \( (n_e) \) and holes occupying the valence band \( (n_h) \) is determined
by the Fermi level $\varepsilon_F$ and the temperature, via

$$dn_{e(h)}(\varepsilon) = D_{e(h)}(\varepsilon) f(\varepsilon) d\varepsilon$$  \hspace{1cm} (1.13)

where $D_{e(h)}$ is the density of states of the electrons (holes) and $f$ is the Fermi-Dirac distribution function given by

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \varepsilon_F)/kT] + 1}$$  \hspace{1cm} (1.14)

thus the only charge carriers present in the dark are those that are thermally excited from the shallow donor (for electrons) or acceptor (for holes) states. Under illumination, the electron density in the conduction bands is greatly increased due to photo-excitations. The Fermi energy describing their distribution must therefore lie close to the conduction band. Analogously, the Fermi energy for holes must lie close to the valence band to account for the increased hole density. Thus under illumination the Fermi level splits into two ‘quasi Fermi levels’ $\varepsilon_{F}^{e}$ and $\varepsilon_{F}^{h}$. The degree of splitting is determined by the illumination intensity, and gives the difference between the chemical potential of the electrons and holes which determines the open circuit voltage,

$$V_{OC} = q (\varepsilon_{F}^{e} - \varepsilon_{F}^{h}).$$

For charge collection, the electrons and holes must reach the cathode and anode respectively, by drift and/or diffusion. At any given point within the active layer, the total current density $J$ is given by the sum of the drift current (first term) and diffusion current (second term) from both electrons and holes

$$J = eE (n\mu_e + p\mu_h) + q \left( D_e \frac{dn}{dx} + D_h \frac{dp}{dx} \right)$$  \hspace{1cm} (1.15)

$E$ is the net electric field felt by the charge carriers resulting from the applied bias and any internal electric fields, $n$ and $p$ are the electron and hole concentration respectively, and $D_e$ and $D_h$ are the electron and hole diffusion coefficients.

This transport process competes with recombination processes occurring either radiatively or non-radiatively. Many different device architectures can be used to facilitate charge collection, either by reducing the distance charge carriers must diffuse, or by optimising the size and distribution of the internal electric field within the active layer. The device structures most commonly used with QD solids are discussed in this section.
1.6.1 Schottky solar cells

The first and most simple device architecture consists of the active layer sandwiched directly between the cathode, often aluminium, and anode, which is most often formed by a transparent film of indium doped tin oxide (ITO). A energy schematic of a typical Schottky device is shown in Figure 1.6. At thermal equilibrium under short circuit conditions, the Fermi levels of all components must align. Assuming a p-type active layer with Fermi level close to the workfunction of ITO, there will be little band bending at the anode. At the cathode, the difference between the Fermi level of the active layer and the workfunction of the metal electrode will cause a flow of electrons across the interface until the Fermi levels are in equilibrium, building up a positive charge at the metal interface and an equal but opposite charge in the semiconductor. Due to the relatively low carrier concentration, the charge in the semiconductor will be distributed over a certain region near to the metal interface. In this region, which is depleted of free majority carriers, the space charge produces an internal electric field evidenced by the bending of the energy levels. The width \( w \) of this depletion region is given by

\[
w = \left[ \frac{2 \varepsilon_0 \varepsilon_r}{eN} \left( V_{bi} - V - \frac{kT}{q} \right) \right]^{1/2},
\]

where \( \varepsilon_r \) and \( \varepsilon_0 \) are the relative permittivity and the permittivity of free space, respectively, \( e \) is the elementary charge, \( N \) is the charge carrier density, \( V_{bi} \) is the

Figure 1.6. Energy levels of a p-type Schottky device. a) At short circuit conditions featuring the most important processes 1) photon absorption 2) recombination (not all mechanisms shown) 3) charge carrier diffusion 4) charge carrier drift 5) charge collection 6) back recombination at the electrode. b) Energy levels at open circuit voltage.
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the built in voltage, $V$ is the applied bias, $k$ is Boltzmann’s constant and $T$ is the material temperature. Beyond the depletion width, the band levels are flat and charge carriers must rely on diffusion for transport. Within the depletion width ($x < w$), the electric field is given by

$$E = \frac{qN_D}{2\varepsilon_0 \varepsilon_r} (w - x),$$

(1.17)

This electric field drives electrons towards and holes away from the cathode, and the Schottky barrier $\Phi_B$ causes diode like rectification of the current $J$ under applied bias $V$, which, for an ideal diode, can be described by the Shockley equation

$$J = J_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] - J_{PH},$$

(1.18)

with $J_0$ the reverse saturation current, $n$ the ideality factor, and $J_{PH}$ the photo-generated current. This equation can be represented by the equivalent circuit shown in Figure 1.7a. For practical devices, contact resistance and a finite mobility lead to a series resistance $R_S$, while back recombination and leakage currents contribute to a parasitic shunt current $J_{SH} = V/R_{SH}$, leading to the non-ideal circuit shown in Figure 1.7b, and the corresponding adaptation of the Shockley equation

$$J = J_0 \left[ \exp \left( \frac{q(V + JR_S)}{nkT} \right) - 1 \right] - J_{PH} - \frac{V + JR_S}{R_{SH}},$$

(1.19)

The reverse saturation current is an important parameter in determining the device performance, and depends on the solar cell structure. For Schottky devices, there are two theories that describe the reverse saturation current.
The first is the thermionic emission theory, which neglects the shape of the Schottky barrier and assumes that all and only charge carriers with energy above the barrier height contribute to $J_0$:

$$J_{0,TE} = J_{00} T^2 \exp\left(\frac{-q \Phi_B}{kT}\right),$$  \hspace{2cm} (1.20)

where $J_{00}$ is the effective Richardson’s constant, equal to 120 A/cm²K². The other theory is the diffusion theory which assumes that the driving force of the dark current is the charge carrier density distribution within the depletion width, given by\cite{52}

$$J_{0,Diff} = e \mu_{e(h)} N_{C(V)} E_m \exp\left(\frac{-q \Phi_B}{kT}\right),$$  \hspace{2cm} (1.21)

where $\mu_{e(h)}$ is the majority carrier mobility, $N_{C(V)}$ is the density of states in the conduction (valence) band, and $E_m$ is the maximum electric field in the device, located at the metal interface ($E(x=0)$). Recently, it was shown by Szendrei et al. that the diffusion theory describes PbS QD devices better than the thermionic emission theory.\cite{53}

The PbS QD layer acts as a dielectric capacitor, with capacitance $C$ given by the Mott-Schottky equation, which allows the doping concentration $N$ to be calculated.

$$\frac{1}{C^2} = \frac{2}{q \varepsilon_r \varepsilon_0 N A^2} \left(V - V_{bi} - \frac{kT}{q}\right),$$  \hspace{2cm} (1.22)

with $A$ the device area defined by the overlap of electrodes.

Because of their simple structure, Schottky devices are ideal for studying the properties of PbS layers, but have several drawbacks for solar cell applications. First, the Schottky junction is formed at the rear metallic contact, but most of the light is absorbed close to the transparent electrode, therefore one of the charge carriers (electrons for p-type layers) must first diffuse to the depletion region where the band bending can facilitate charge extraction, making them more susceptible to recombination. Secondly, the open circuit voltage in Schottky devices is limited to $\sim0.67E_g/e$ and in practice even less, due to pinning of the Fermi level to trap states at the metal-semiconducting interface.\cite{48} Finally, the Schottky junction poses only a small barrier to charge carrier re-injection from the metal (process 6 in Figure 1.6), leading to low shunt resistance.
1.6.2 Heterojunction solar cells

The Schottky barrier can largely be removed by inserting a second semiconductor at the metal interface with Fermi level close to the metal work function. Often this is done using a wide bandgap highly n-doped oxides such as TiO\textsubscript{2} or ZnO. The n-type semiconductor should form a so called type-II heterojunction, where the bandgaps are staggered. The difference in Fermi levels causes band bending between the oxide and active layer which facilitates charge transport, see Figure 1.8a. The depletion width of this p-n junction is given by\textsuperscript{[54]}

\[
w = \left[ \frac{2\varepsilon_r\varepsilon_0}{q} \left( \frac{N_A + N_D}{N_A N_D} \right) (V_{bi} - V) \right]^{\frac{1}{2}},
\]

(1.23)

with \(N_A\) and \(N_D\) the acceptor and donor concentrations in the p and n type material, respectively, and \(V_{bi}\) the p-n junction bias given by

\[
V_{bi} = \frac{kT}{q} \ln \frac{N_A N_D}{n_i^2},
\]

(1.24)

where \(n_i\) is the intrinsic (undoped) carrier concentration. The distribution of the depletion region across the junction is governed by the ratio of doping concentrations. Charge conservation requires that the total charge in the space charge region on either side of the junction is equal, or

\[
N_A w_p = N_D w_n.
\]

(1.25)
where $w_p$ and $w_n$ are the fraction of the total depletion width $w$ located on the p- and n-side of the junction, respectively.

Because the doping concentration of the oxide is typically much higher than that of the PbS, the depletion region is located mostly in the PbS layer, which facilitates charge collection. In addition, the high ionisation potential of the oxide layers renders them very stable in air so they can effectively encapsulate the PbS layer, increasing device stability. In addition, the transparent oxide can be used as an optical spacer to optimize the distribution of light within the solar cell by controlling the oxide thickness.\[20,55]\]

In an alternative configuration, the transparency of the oxide allows it to be placed at the front cathode, in which case the rear contact, usually gold, is required to align with the Fermi level of the active layer. The overall effect of this configuration is that the polarity is inverted; harvesting electrons from the transparent electrode and holes from the rear metallic contact. This configuration has three advantages; the light enters at the side where band bending is greatest, which enhances the charge collection efficiency, and the gold electrode both protects the active layer and is itself much less prone to oxidation than the low work function electrode required for the non-inverted structure, resulting in much higher stability. Finally, the large bandgap oxide acts as a more effective selective contact, blocking charge carriers (holes in the examples in Figure 1.8) from collection at the wrong electrode.

\[1.6.3 \text{ \ Pn-junction solar cells} \]

With the realisation of n-type PbS layers using halide anion ligands, it is possible to create PbS/PbS p-n junctions. The equation for the depletion width is the same as for the case of a heterojunction (Equation 1.23), but because doping concentrations are similar, the depletion region is distributed more equally over both layers, in accordance with Equation 1.25. This junction can be used in combination with a heterojunction, allowing the band bending to be extended further into the active layer (Figure 1.9), making thicker layers and therefore more light absorption possible.

\[1.6.4 \text{ \ Tandem solar cells} \]

The Shockley-Queisser limit described in Section 1.1 applies to solar cells with a single semiconductor acting as the active layer. It is possible to over-
come this limit by intelligently connecting two or more solar cells with different bandgaps such that the connecting interlayer acts as a recombination centre for electrons from the first subcell and holes from the rear subcell.

Using a semiconductor as the front sub-cell with bandgap wider than in the ideal single junction case, high energy photons are harvested with lower thermalisation losses. As the rear subcell, a narrow bandgap material is used to collect the transmitted low energy photons and reduce absorption losses. Figure 1.10 displays the energy level diagram of a normal (non-inverted) tandem solar cell, and the device mechanisms will be explained according to this architecture.

The necessary recombination at the interlayer of equal numbers of charge carriers from both subcells imposes a limit of the total current extracted from the device to the lowest of the two subcell currents. For this reason, balancing
The current generated by the subcells is crucial to avoiding unnecessary losses in tandem solar cells. This can be done by carefully varying the thickness, and thus the photoabsorption, of the respective layers such that an equal current is collected from each. The recombination in the interlayer also pins the quasi Fermi levels the electrons and holes from the front and rear subcells, respectively. The resulting $V_{OC}$ of the tandem device is thus the sum of the individual $V_{OC}$’s in accordance with Kirchoff’s law for series-connected solar cells. The detailed balance limit of a double junction solar cell is 45.7%, making tandem solar cells an interesting alternative to the single junction architecture.

### 1.7 Thesis outline

This thesis focuses on the device physics of PbS QDs in electronic devices and the fabrication and optimisation of solar cells with various structures. **Chapter 2** focuses on the fabrication of tandem solar cells featuring PbS QDs in combination with a blend of P3HT and PCBM. We successfully introduce a new Al/WO$_3$ interlayer to fabricate tandem solar cells with an efficiency of ~2%, utilizing a broad absorption range. In **Chapter 3** we present the use of PbS QDs with a thin shell of CdS as an alternative strategy for trap passivation. We observe increased $V_{OC}$ in Schottky solar cells, and show that this is due to a reduction of the trap density near the conduction band. **Chapter 4** is devoted to the study of the temperature dependent properties of PbS solar cells and films. We fabricate p-n junction solar cells with an efficiency of ~9% and measure the temperature dependent behaviour. We observe increased efficiency at lower temperatures, particularly due to increased $V_{OC}$ and $FF$, without degradation of the $J_{SC}$. We explain this trend by measuring the temperature dependence of the most important film properties, and give some guidelines for further enhancement of the solar cell efficiency at room temperature. Finally, in **Chapter 5** we demonstrate a method to dope EDT-capped PbS films by altering the Pb/S ratio on the PbS surface. We find that p-n junction solar cells demonstrate higher $J_{SC}$ and $FF$, with approximately equal $V_{OC}$, leading to improved overall efficiency. The reason for this is traced back to an increased doping concentration of the EDT-capped PbS film.
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References

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