Wrocław University of Technology

Type III solar cells based on quantum dots

BACHELOR'S THESIS

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October 6, 2019

Abstract

In this thesis the extensive study of possible and surly optimal materials for Quantum Dot Solar Cells (QDSCs) will be provided to the reader. One will have the opportunity to develop a rather current image of the necessary parts in their architecture which will be supported with an abundant description of the important aspects in engineering a photovoltaic device. With an introduction of its kind we will try to convey a basic but sufficient knowledge of standard terms, light with matter interaction, light spectrum analysis, quantum dots description with their behaviour and a photovoltaic device operation theory with certainly needed quantities that one has to find in order to properly describe a solar cell. In many parts we will try to outline possible enlargement of that information. With the objective of creating a possibly competitive QDSC the description of methods that we used will be included with a related to them characteristics. One will also be able to use this paper as a review of today's development phase and current technological state of the other scientific groups all around the world. After a successful development of a solar cell, the analysis and comparison will definitely be provided.

Dedication

I would like to dedicate ...

Declaration

I hereby declare that the present bachelor's thesis was composed by myself and that the work contained herein is my own. I also confirm that I have only used the specified resources. All formulations and concepts taken verbatim or in substance from printed or unprinted material or from the Internet have been cited according to the rules of good scientific practice and indicated by footnotes or other exact references to the original source.

The present thesis has not been submitted to another university for the award of an academic degree in this form. This thesis has been submitted in printed and electronic form. I hereby confirm that the content of the digital version is the same as in the printed version. I understand that the provision of incorrect information may have legal consequences.

(Signature)   (Place, Date)

Acknowledgements

Thanks

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Chapter 1

Introduction

We, as a society nowadays, are in constant demand for energy. Although, even with the development of calculating, conducting and studying it, we don't really know what the energy is, we are depending on that abstract quantity. One might probably say that to study physics is to endure to study energy in its every possible form. There's a brilliant quote from Bill Bryson that: "Energy is liberated matter, matter is energy waiting to happen." What might be incredible is that from this strictly mathematical quantity we can deduct anything. And what's also important it is as arbitrary as it gets, depending only on one's reference. From energy we can create few more important quantities such as *power* P, which is simply the energy provided per unit time, so:

$$E = \int P\left(t\right) dt$$

The energy will be represented in J (Joules) or eV (electron volt), which directly describes energy of elementary charge body ($e \approx 1.602 * 10^{-19} C$) in 1V (Volt) potential.

$$1eV = 1.602 * 10^{-19} J$$

Power will be then represented in W (Watts) ($W = \frac{J}{s}$).

The rise of energy consumption has proven that in the future we will almost certainly require even more. From Global Energy Perspective paper [5] we can learn that:

- Global energy demand will reach plateau at around 2035 despite strong population expansion and economic growth thanks to emphasis on renewable sources, more efficient service industries or more efficient industrial regions

- The energy demand and economic growth became "decoupled" for the first time in history

- Renewables will provide more than half the electricity after 2035

The reader is strongly recommended to take a look at the document.

With saying that we can produce energy there's a slick trick given with the phrase. Energy cannot be simply created, it is just converted from another source so nothing is ever lost or miraculously made. The problems we need to struggle

with are then being able to obtain as much energy from the energy source as it is possible and of course, as humankind society is governed by money, keep the cost lowest. There is plenty of different energy sources that we learned to receive energy from. In Figure 1.1 we can see the most vivid ones nowadays. But with the human demand fulfilment come great damages and soon depleting resources of many energy sources such as fossil fuels.
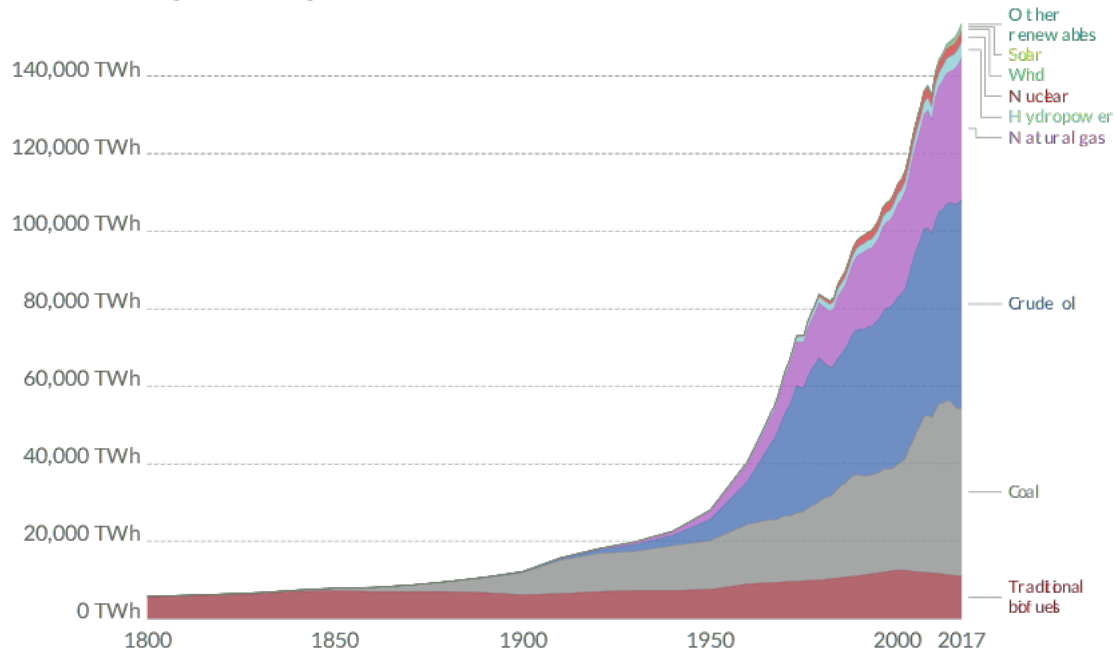
Figure 1.1: Energy sources contribution in world scale [3]

The necessity of searching new possible ways to harness it through renewable sources has become a global issue. Our concern of the environment had never been that serious before. Not only the change of methods for energy production must be enhanced because of this demand but we need to be strictly aware of the World's urging trepidation of Global Warming of which evidence is provided for example here [10].

Among all of the ideas created in a past few decades, solar energy is believed by many to be the most reliable and promising. It can be directly converted into electricity, heat or chemical energy and our only star seems to be an infinite power resource for us. In the last ten years the world solar PV electricity production has grown impressively, being almost three times bigger in 2016, than in 2010 [11]. In theory, the Sun has the potential to fulfil earth's energy demand if it is not for the technology. Annually, nearly 10^{18} EJ of energy reaches our planet and of that 10^4 EJ is claimed to be harvestable. The possibility of converting the solar energy into electric energy has been studied since discovery of the basic photovoltaic effect and the development of semiconductor technologies.
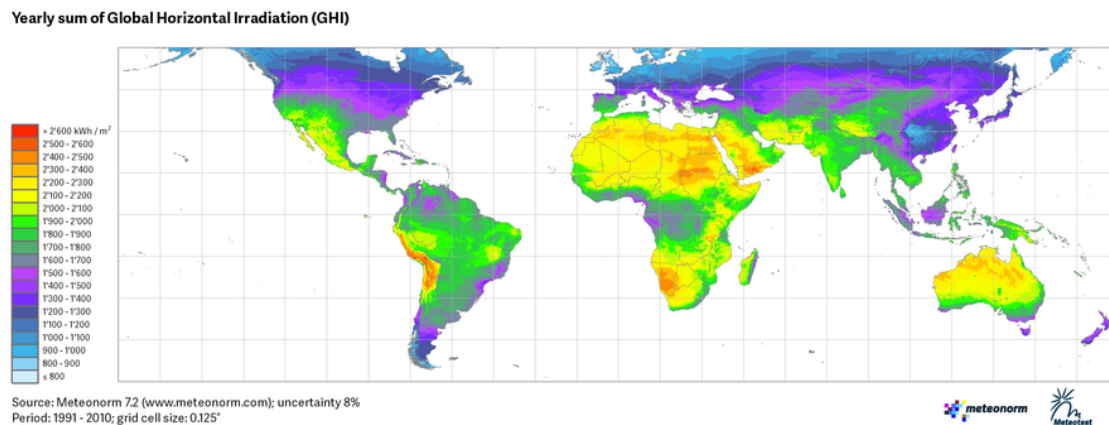
Yearly sum of Global Horizontal Irradiation (GHI)

Source: Meteonorm 7.2 (www.meteonorm.com); uncertainty 8%
Period: 1991 - 2010; grid cell size: 0.125°

Figure 1.2: Annual yearly sum of Global Horizontal Irradiation [8]

Chapter 2

Theory

With this chapter the introduction of some theoretical concepts will be provided. Certainly some of chapters below could be omitted without missing the final result and its meaning. Nevertheless, even if the paper is laced with rather practical analysis and effects, a physicist should be sure to understand the aspects of an experiment well, not just to have a better insight into the outcome but also to be sure that during the process no foolish mistakes are made and to be able to find new methods to improve the research. Therefore, few parts will just be a reminder and introduction to notation used or to ensure the understanding and some will be treated as an inquiry of what might be searched to describe it further.

2.1 Classical and semi classical theory of light and light with matter interaction

As in the photovoltaic physics we are constantly struggling with light itself we should be know what the light actually is and how it interacts with matter in many, rather curious and different ways. Why is that so that matter looks the way it does and what of its properties can we control. In this chapter we will embrace the phenomena just to create an image of what we are dealing with.

2.1.1 Basic properties of electromagnetic field

Before we actually begin we need to state some classic information about the physics of electric charges. The electromagnetic field is represented by two generally complex vectors, even though the physical result that we are expecting is ought to be real. Those vectors are $\mathbf{E}$ – *electric field* and $\mathbf{B}$ – *magnetic induction*. The properties of those fields are of course described by the *Maxwell's equations*. For them we shall also introduce two more important quantities ρ – *the electric charge* density and $\mathbf{j}$ – *electric current density* vector. We can define them in this way:

$$e = \int \rho dV \tag{2.1.1.1}$$

$$I = \int_S \mathbf{j} \cdot \mathbf{dS} \tag{2.1.1.2}$$

Where I is electric current.

The four Maxwell equations in differential form are:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \rightarrow \textit{Faraday's induction law} \qquad (2.1.1.3)$$

$$\nabla \times \mathbf{B} = \mu_0 \left(\mathbf{j} + \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) \rightarrow \textit{Ampere's circuital law} \qquad (2.1.1.4)$$

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} \rightarrow \textit{Gauss's law} \qquad (2.1.1.5)$$

$$\nabla \cdot \mathbf{B} = 0 \rightarrow \textit{Gauss's law for magnetism} \qquad (2.1.1.6)$$

To freely describe the properties of the fields interacting macroscopically with material objects we here we can also introduce standard auxiliary fields with polarization and magnetisation of a macroscopic medium. Those vectors are $\mathbf{D}$ − *the electric displacement* and $\mathbf{H}$ – *the magnetic vector*. From Gauss's law for magnetism there is a straight implication that no magnetics monopoles exist and Gauss's law may be also treated as electric charge density definition.

$$\mathbf{D}\left(\mathbf{r},t\right) = \epsilon_0 \mathbf{E}\left(\mathbf{r},t\right) + \mathbf{P}(\mathbf{r},t) \qquad (2.1.1.7)$$

$$\mathbf{H}\left(\mathbf{r},\,t\right) = \frac{1}{\mu_0}\mathbf{B}\left(\mathbf{r},\,t\right) - M(\mathbf{r},\,t) \qquad (2.1.1.8)$$

Where $\mathbf{P}$ is a *polarization vector* and $\mathbf{M}$ is *magnetization vector*.
And with them our former equations change to:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \rightarrow \textit{Faraday's induction law} \qquad (2.1.1.9)$$

$$\nabla \times \mathbf{H} = \left(\mathbf{j} + \frac{\partial \mathbf{D}}{\partial t} \right) \rightarrow \textit{Ampere's circuital law} \qquad (2.1.1.10)$$

$$\nabla \cdot \mathbf{D} = \rho \rightarrow \textit{Gauss's law} \qquad (2.1.1.11)$$

$$\nabla \cdot \mathbf{B} = \mathbf{0} \rightarrow \textit{Gauss's law for magnetism} \qquad (2.1.1.12)$$

If we put divergence on the Ampere's law, we can then place Gauss's theorem in the equation because of the exchangeability of partial derivatives and from that we can simply derive so called equation for *charge conservation:*

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = \mathbf{0} \qquad (2.1.1.13)$$

The field is said to be static if all quantities are independent of time and, of course, no currents are present. This is the special case but we cannot be so lucky every time. Optical fields are usually sources of very rapid time variety but one may deal with it thanks to the possibility to average the field over macroscopic time interval which is mostly the case in for photovoltaic needs, where for example the light source is a distant star.

Relations for substances under influence of those fields can be very complicated. There is a special case that can make life easier as well. If the material is *isotropic* (all its properties are identical in every direction) they take a simple form of:

$$\mathbf{j} = \sigma\mathbf{E} \rightarrow Ohm'slaw \qquad (2.1.1.14)$$

$$\mathbf{D} = \epsilon\mathbf{E} \qquad (2.1.1.15)$$

$$\mathbf{B} = \mu\mathbf{H} \qquad (2.1.1.16)$$

Here σ is called *conductivity*, ϵ is a *dielectric constant* and μ is *magnetic permeability*. Normally, all of those are tensors. In the case of scalar conductivity we can separate macroscopic media in three different categories: conductors, semiconductors and isolators. The same goes for magnetic permeability. With $\mu < 1$ the substance is said to be diamagnetic, $\mu > 1$ paramagnetic and so with $\mu \gg 1$ ferromagnetic. Obviously this description is rather intuitive and treated as a general theory. For example for exceptionally strong fields the area of non-linear optics is needed to be got into which provides higher power terms of fields in the above equations. Also, the case where we need to include relativistic effects by extracting previous values of E acting on charges is not included as well. The information will be expanded later when needed ,but if the reader wants to really expand following discussion understanding, it can be done via [2] [6].

2.1.2 Boundary conditions at discontinuity

2.1.3 Energy of electromagnetic field, the Poynting vector

2.1.4 Wave equation

2.1.5 Scalar waves and wave packets

2.1.6 Vector waves

2.1.7 Refraction and reflection of classical electromagnetic wave

2.2 Physics and properties of solids and semiconductors

2.2.1 Physics and properties of solids

The most common distinction between solids is taking their resistivity as a criterion. We can distinguish three main categories for them - metals, semiconductors and isolators. Within that we can also provide temperature differences beneath them as for the metals, the resistivity goes down with the temperature increase and for the rest of them it is quite the opposite.

Also, as it will be later extended, when we light a semiconductor or an isolator we can clearly observe so called *absorption threshold*.
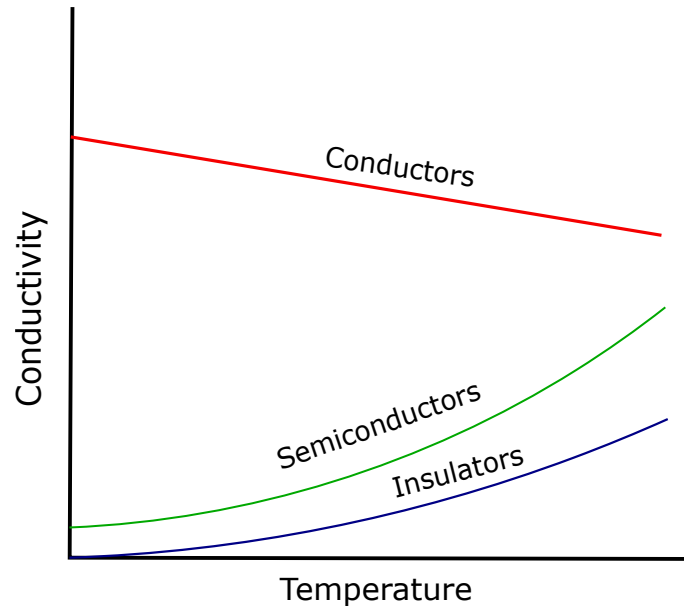
Figure 2.1: Demonstrations of conductivity behaviour of different types of solids

2.2.2 Drude model of free carriers

The discovery of electron in 1897 had the great impact on the first attempt to describe properties of solids. Fairly early, just three years later, Drude constructed his first theory which based on the usage of quite successful kinetic theory, which described the behaviour of gases. Starting with metals he imagined a gas of electrons which are identical solid spheres moving randomly in straight lines. They change directions by collisions and of course no other forces than that of the very quick collisions are taken into account. As metals are neutral, Drude deduced that much heavier and steady particles are compensating negative electron charge. Strictly, that kind of model provides us with the crystal structure but back then, Drude assumed (and for great deal of metals it's fairly true), that only valence electrons are important and they move freely through the whole metal. The basic assumptions for the model are:

1. Between collisions, interactions electron-electron and electron-ion are able to be neglected. The first one is called *independent electron approximation* and the second is called *free electron approximation*.

2. Only the collisions are important. They are approximately instantaneous

events that alter the velocity of the electron. The electron-electron scattering is one of the least important scattering mechanisms in metals. Nevertheless with others, very often, in describing conducting electrons it is not important to describe all mechanisms deeply.

3. We can assume that the period in which an electron isn't making any collision is τ *(relaxation time)* and thus the probability that electron is undergoing a collision in any infinitesimal time period dt is $\frac{dt}{\tau}$. This of course means that τ is average time and it is independent of both velocity and position $\rightarrow$ therefore also time.

4. Thermal equilibrium is achieved only through collisions.

Electrical Conductivity

Drude model can describe, with certain accuracy, the Ohm's law $V = IR$. Resistance R is a quantity which is dependent of the dimensions of the material, therefore resistivity, which has been mentioned before can be used.

$$\mathbf{E} = \rho \mathbf{j} \tag{2.2.2.1}$$

The current density j is the same as in former section, when we were describing Maxwells equations. If n electrons move with velocity $\mathbf{v}$ in time period dt and through area A we get that charge connected with that quantities is $-nevAdt$ so current density is:

$$\mathbf{j} = -ne\mathbf{v} \tag{2.2.2.2}$$

and is just a net current because of random electron movement. Also, let's assume that electron has a velocity $\mathbf{v_0}$ at time t_0 just after a collision and additional velocity $\frac{-\mathbf{E}e\tau}{m}$ from the external field, we can take average through long time period. The random velocity $\mathbf{v_0}$ disappears and therefore, connecting with 2.2.2.2 we get that:

$$\mathbf{j} = \sigma \mathbf{E} \tag{2.2.2.3}$$

$$\sigma = \frac{ne^2\tau}{m} \tag{2.2.2.4}$$

This tells us about the linear dependence of $\mathbf{j}$ on $\mathbf{E}$. Note that $\tau = \frac{m}{\rho ne^2}$ because $\tau = 1/\rho$ where ρ is *resistivity*. Drude model was a first and simple model used in describing solid state materials. As simple as it is, it can yet provide some accurate results. Even more can be read in [9]

Chapter 3

Cell architecture

Chapter 4

Depositions and parameters

Chapter 5

Results

5.1 First device deposition

A first insight of what can we do and what would be the challenges to overcome has been made due to creation of a first working solar cell. The cell was based on PbS QDs and it has shown a promising quantities for further development. The whole paper provides a comparison of Vimun silicon solar cell and our own QDSC.

5.1.1 PbS Quantum Dot Solar Cells

The whole idea of all-solution processed QD solar cells is beginning to mark its footprint in modern photovoltaics. Within all of type III SC PbS QDs are promising candidates and certainly a field of quick improvement. Yet, what is so promising about them and what are the features that distinguish them from other types. In case of PbS QDs it must be denoted that the main advantages that they provide are the high efficiency and wide bandgap tunability due to its direct link with quantum dot size. For photovoltaic purposes the next important thing would be th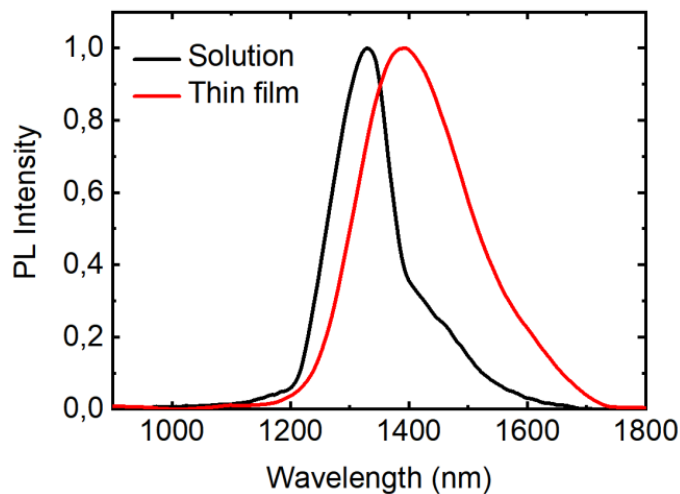e ability to multiple excitation through the band gap. They are used in many different structured solar cells, creating a numerous variations of junctions and quantum dot treatments and achieved over 11% power PCE as for last few years. The main problems with them would be to conduct and choose a fine ligand passivation. In our case the halide anions from precursors of tetrabutylammonium iodide (TBAI) and 1,2-ethanedithiol (EDT) were used. Ligands from such precursors do not only, more or less precisely, passivate surface defects, which are of course bad for our case, but modify electronic

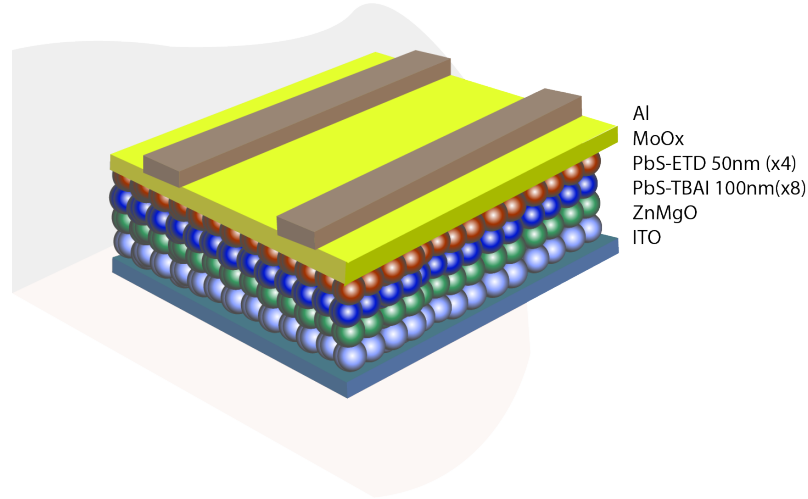Figure 5.1: Emission spectrum of PbS QDs [1]

Figure 5.2: 3D structure of the device

properties of QDs as well. The PbS-EDT layer was used as hole transport and
PbS-TBAI, a main light harvesting layer, has been reported to usually be a n-type
semiconductor, probably owing to a) I¬ anions that are exchanged in PbS QDS with
S¬2- and b) I- anions are bound to the surface and repulse a oxidative processes.
The choice of those were due to rather improved stability of QDs comparing to
other layer passivating (devices with TBAI and EDT bi-ligands have been shown to
provide a much longer stability in air than others). Although a longer air-exposure
provides undesirable consequences that downgrade the cell significantly, the short
period exposure is suspected of creating a more efficient charge extraction. Never-
theless, the inner processes that allow that bi-layer structure to be one of the best,
provided for those types of QDSCs, is still eluded and further improvements are
expected if it becomes much more understood. For example, a greatly simplified
deposition has been achieved by replacing methanol with acetonitrile, which conse-
quently improved electrical properties of photovoltaic device as well. (The device
structure was very similar to ours). There are irrefutable results in achieving fine
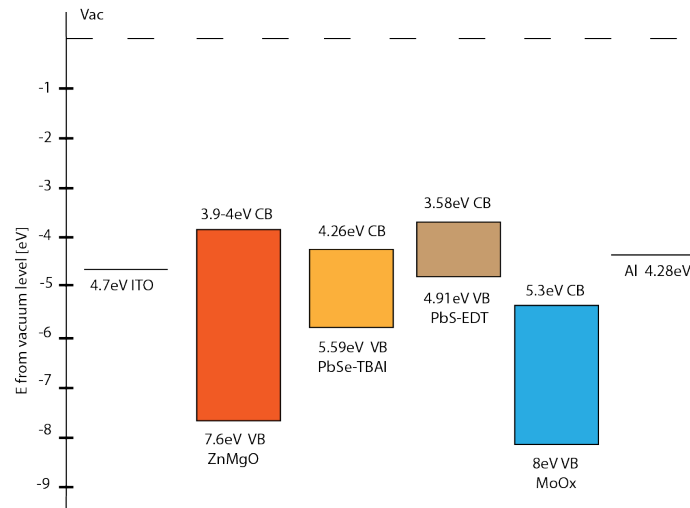results from synthetisation from the group. [12] [4]

Figure 5.3: Energy structure of QDSC

5.1.2   Device fabrication

The support for a whole device was ITO-coated glass substrate that was cleaned with strong solvents and drained ultrasonically. After that a double layer of MgO was created by using a spin-coater and after annealing PbS QDs were fabricated using spin-coating as well. It is important to denote, that it was possible to create a multi-deposition layers of QDs, which means the structure isn't eluted from the ground. The layers were successfully dried in vacuum. After that, a MoOx firm has been added for creating inside trapping states and with sputtering process Al contacts were created on the device. As many heavy-metal QD semiconductors are toxic and degrade in air they must be also encapsulated in a stable polymer shell to avoid exposure.

Figure 5.4: Device and Quantum-Dots produced in our lab
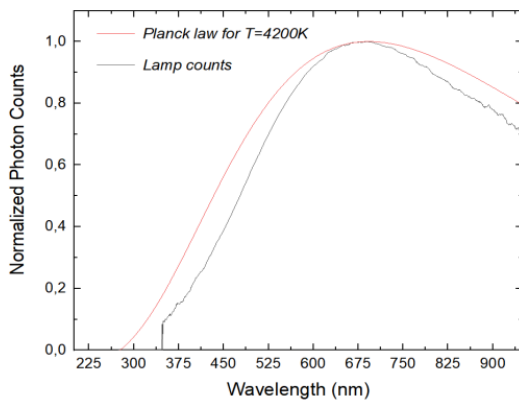
5.1.3   Results

Figure 5.5: Comparison of Black Body photon counts and that of our light source

From the following calculations we were able to compare both of the solar cells to distinguish what shall be definitely improved to achieve better effects. Standard photovoltaic measurements were provided to create IV both IV characteristics. However, it has to be denoted that neither were the surfaces of both devices the same, nor were the lengths from the light source.

Therefore a certain calculations and assumptions were made. From the photo-diode detector which were illuminated from the light source from $h_d = 400mm$ we calculate the P_d-power on the detector. We know that the photo-diode responsivity:

$$R_\lambda = \frac{I_p}{P} = \frac{I_p}{r_p \cdot \frac{hc}{\lambda}} \qquad (5.1.3.1)$$

where I_p is a photocurrent output, and P is a ratio of radiant energy incident on the photodiode, which directly enables to calculate r_p- photon flux(number of photons/sec). We also define quantum efficiency of a photodetector as:

$$\eta = \frac{r_e}{r_p} \qquad (5.1.3.2)$$

which is the number of light created electrons to number of incident photons. That depends on wavelength through absorption coefficient, thickness of layers etc. Therefore we can say that:

$$r_e = \eta r_p = \frac{\eta P}{\frac{hc}{\lambda}} \to I_p = \frac{e\eta P}{\frac{hc}{\lambda}} \qquad (5.1.3.3)$$

Therefore, responsivity may be written as:

$$R_\lambda = \frac{e\eta P}{hc} \qquad (5.1.3.4)$$

According to those calculations we now see that from:

$$J_{sc} = e \int_\lambda \Phi_p(\lambda) \cdot \eta(\lambda) d\lambda \qquad (5.1.3.5)$$

Φ_p- is a photon flux now, for the sake of new calculations to distinguish the difference of photon counts and J_{sc} is a short-circuit current. From that of above we now can see that:

$$J_{sc} = \int_\lambda \Phi_p(\lambda) \cdot R_\lambda \cdot \frac{hc}{\lambda} d\lambda \to \qquad (5.1.3.6)$$

$$J_{sc}^{rel} = \int_\lambda \Phi_p^{norm}(\lambda) \cdot R_\lambda \cdot \frac{hc}{\lambda} d\lambda \qquad (5.1.3.7)$$

where we have used relative value for short-circuit thanks to using a normalised values because of the fact that detector isn't ideal and that we can calculate the number of incident photons by simply using:

$$N_p = \frac{J_{sc}}{J_{sc}^{rel}} \qquad (5.1.3.8)$$

From now we can clearly say that:

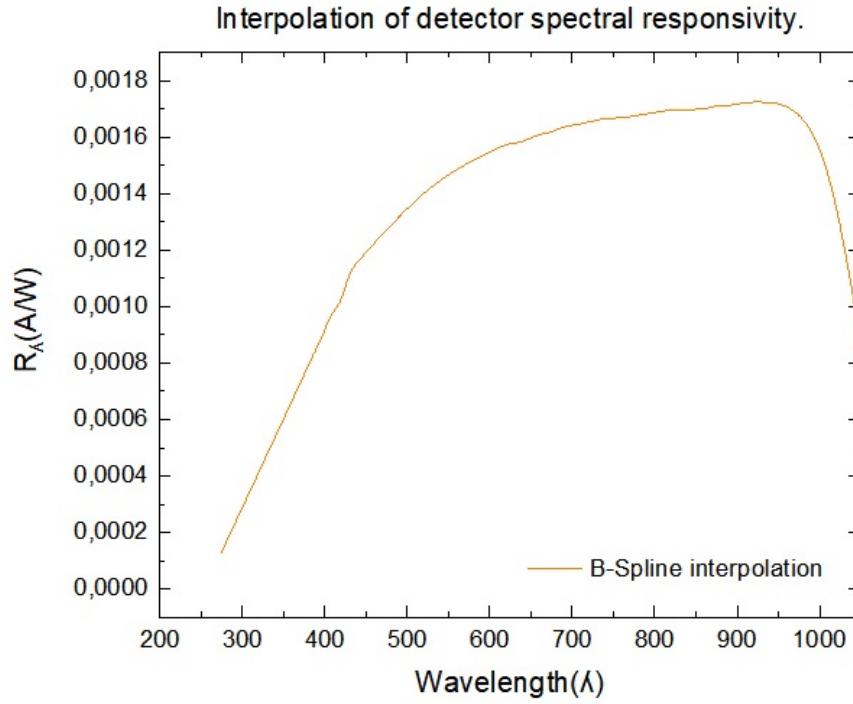$$P_d = \int_\lambda \Phi_p^{norm}(\lambda) \cdot N_p \cdot \frac{hc}{\lambda} d\lambda \qquad (5.1.3.9)$$

Figure 5.6: . Original data from Gigahertz Optik Gmbh

From integration and minding that $J_{\text{sc}} = 3,5 \cdot 10^{-4}$ mA we achieved that:

$$N_p \approx 1,73 \cdot 10^{24}$$

$$P_d \approx 0,23\,(W)$$

The calculations are very roughly approximated and are just a presentation of methods used, mainly due to the fact that the full spectral characteristics weren't absolutely known. We can now estimate $P_{\text{density}} \approx \frac{P}{\Omega}$, where Ω is a solid angle. Therefore in our case from the information from 5.1 we can calculate PCEs of both photovoltaic devices by using:
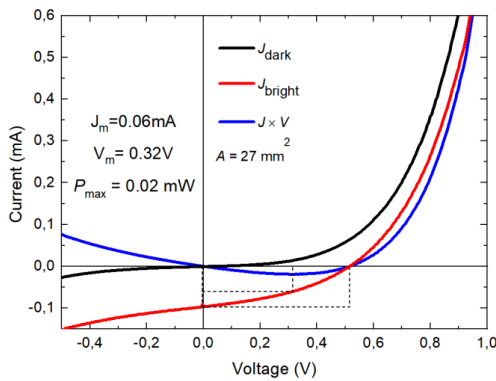
(a) QDSC
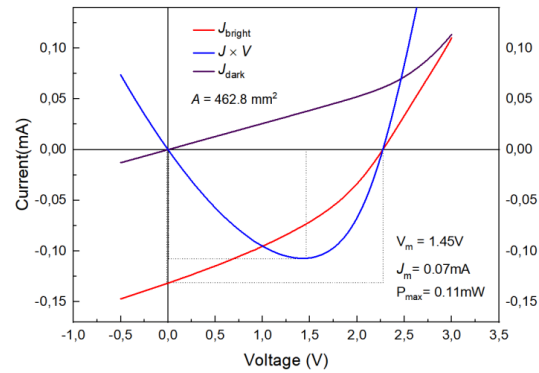
(b) Commercial solar cell

Figure 5.7: IV characteristics for QDSC and commercial cell

	Detector	QDSC	Commercial Cell
Length from light source[mm]	400	75	603
Surface[mm^2]	36,32	27	462,8
Solid angle[sr]	2,27E-04	4,80E-03	1,27E-03
Incident Power [W]	2,30E-01	5,75E-03	1,53E-03

Table 5.1: Parameters of tested solar cells

$$PCE = \frac{V_m J_m}{P_{\text{in}}} \tag{5.1.3.10}$$

	V_m[V]	I_m[A]	P_{in}[W]	PCE
QDSC	0,32	6E-05	5,75E-03	0,33%
Commercial Cell	1,45	7E-05	1,53E-03	6,65%

Table 5.2: PCEs of photovoltaic devices

Provided that producer of the Commercial Cell provides similar PCE compared to the given in 5.2 and the efficiency of our light source is aimed to be close to 10%, and therefore its power is 150W we get circa 15W of light which we get by multiplying the power on the detector by a factor of $4\pi/\Omega$, where Ω is the solid angle for the detector. This means that our, certainly course, calculations show reasonable results from which we can definitely draw some conclusions.

5.1.4 Conclusions and future prospects

As we can clearly see, the PCE of QDSC made is small compared to the current world efficiencies [7]. This can be caused by numerous reasons. Working with colloidal quantum dots is always connected with the careful arrangements of various parameters. The slightest change of just one may provide a drastic change in the final result. Therefore we may conclude that the reason of such an efficiency is mostly challenged by the optimal choice of the layer width, quick degradation of QDs in the presence of air or physical defects on the device structure. The large leakage current may suggest that there are many defects inside the device structure which simply create traps for moving electrons. Nevertheless, the prospect of creating competitive QDSC is definitely in our reach. For example, we can see that V_{oc} is really large for device with such a small surface. Now, we have to deal with the improvement of our device. Optimization of the layer width and enlarging of CQDs stability will be the first things to do, but certainly not last. After testing those aspects, we may check if there is another way to exchange ligands in CQDs, which may provide major improvement in mobility, if there is growth of efficiency when changing or adding another transport layer in the device structure or if layer homogeneity can be further increased to stay comprehensive and competitive.

Chapter 6

Future possibilities

Chapter 7

Conclusion and outlook

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