Master's Thesis

Camera based electroluminescence measurements of perovskite solar cells.

A thesis presented for the degree Master of Science.

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Contents

1 Introduction

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2 Theory of Electroluminescence

This chapter explains the theoretical background of Electroluminescence (EL). Starting with the rate of radiating recombination, depending on the material's band structure (see section XY). The rate depends on the carrier concentration, so section XY explains the carrier density profile. Section XY ends with the light path of the radiation out of the sample.

2.1 Rau's relationship

The basis for our discussion of EL emission is the relationship given by Rau (2007):

$$\frac{d\Phi}{d\vec{r}}(\vec{r}) = \alpha(\vec{r}) \, n(\vec{r})^2(\vec{r}) \, \Phi_{BB} u(\vec{r}).$$ (2.1)

Because all the volume elements $dV(\vec{r})$ contribute to the emitted photon flux we integrate the photon flux:

$$\Phi_{em}(\vec{r}_S, \Omega_S, E_\gamma) = \int T(\vec{r}, \vec{r}_S) \, \alpha(\vec{r}) \, \Phi_{BB}(E_\gamma) \, u(\vec{r}) \, d\vec{r},$$ (2.2)

for the electromagnetic flux at $\vec{r}_S$, into spacial angle Ω_S at photon energy E_γ. Inserting Donolato's reciprocity theorem (?) for $u(\vec{r})$ yields (CITE):

$$\Phi_{em}(\vec{r}_S, \Omega_S, E_\gamma) = \int T(\vec{r}_s, \vec{r}) \, \alpha(\vec{r}) \, fc(\vec{r}) \, d\vec{r} \, \Phi_{BB}(E_\gamma) \left[\exp\left(\frac{qV}{kT}\right) - 1\right].$$ (2.3)

2.2 The Principle of detailed balance

W. van Roosbroeck and W. Shockley presented 1954 the principle of detailed balance, showing the relation between the rate of radiative recombination and optical properties, such as the absorbtion coefficient α (CITE).

3 Perovskites and perovskite solar cells

This chapter gives an overview over the material perovskite, it's properties and current research, and perovskite solar cells. PSCs consist of several materials, each providing specific functionalities and need to be chosen accordingly to the perovskite.

3.1 Perovskite materials

3.2 Perovskite Solar Cells

4 Setup

This chapter presents the experimental setup for electroluminescence measurements. Successful EL measurements consist of injecting charges into the recombination layer, charges recombining and detecting the emitted luminescence. Therefore, section 4.1 explains the general setup used for EL measurements. section 4.2 explains the Perovskite Cell layout and electrical contacting of the cells, which is used to inject charges into the perovskite layer. Optics focus and a camera measures the EL intensity (see section 4.3). The chapter concludes with the consideration of noise and measurement errors.

4.1 General Setup

The setup is enclosed in a black housing, shielding the inside from outside light and noise (see Figure 4.1). All parts inside the chamber are painted black to minimize internal reflections and thereby the detection of stray light. A vacuum pump, voltage source, multimeter and operating table with a computer are connected to the setup from the outside, providing further utility. Inside the enclosure are the probe holder and the camera. The camera is mounted on rails and can be moved in three dimensions, enabling position according to used optics and samples.

4.2 Electrical Connection

Perovskite Solar Cells (PSCs) are manufactured on 25 mm x 25 mm glass substrates (see Figure 4.2). Four cells are deposited on one substrate, each single cell having an active area of 4 mm x 3.5 mm. The cell stack consists of a 0.7 mm thick glass substrate, with a 100 nm thick layer of indium tin oxide (short ITO) deposited on top. The ITO is structured by laser ablation, isolating individual cells from each other. Onto the ITO, 10 nm of 2,2',7,7'-Tetra(N,N-di-p-tolyl)amino-9,9-spirobifluorene (short: Spiro-TTB) is deposited as a hole transport layer (short: HTL), followed by 500 nm of methylammonium lead triiodide (short: MAPI) as the absorbing material. The top side of the MAPI is contacted with 8 nm of fullerene (short: C_{60}) and 23 nm bathocuproine (short: BCP), acting as the electron transport layer (short ETL). In the end of the fabrication process, 100 nm Gold are deposited by thermal vapor deposition on top of the ITO and the C_{60} and BCP. To successfully contact the PSC a holder with four pins is used. The PSC is positioned face down, with the glass substrate above, onto the holder, positioning the gold pads on all contacts. The holder uses two pins to check proper contacting of the PSC and the other two to source voltage.
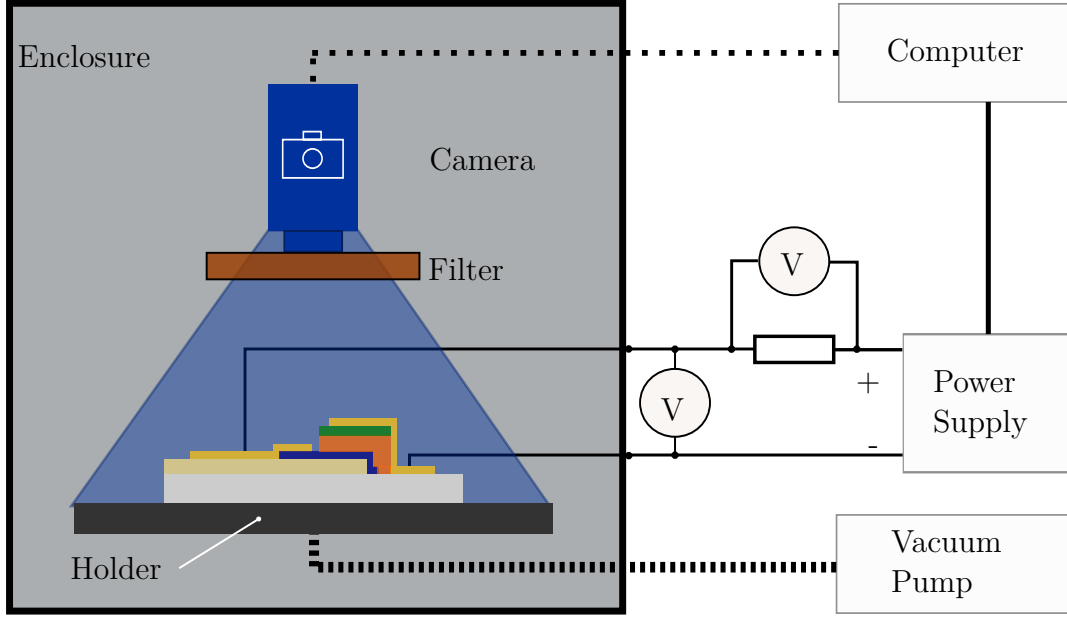
Figure 4.1: Schematic of the EL measurement setup. Camera and Probe are positioned inside the enclosure, and the computer, power supplies and measurement devices are provided from the outside. Two multimeters are used to measure the voltage drop and current sourced.
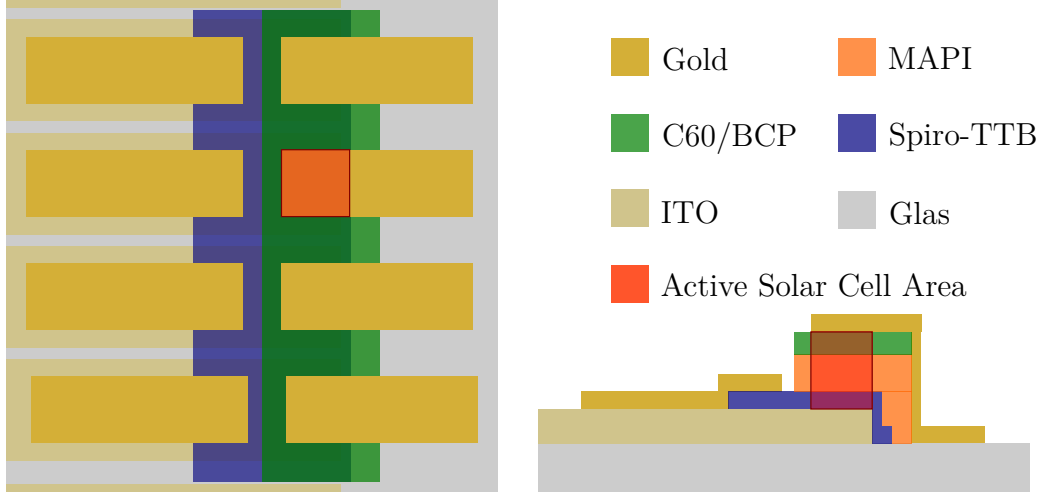

Figure 4.2: Schematic layout of the perovskite solar cell. Not to scale.

The holder is electrically connected to a power supply[1], in series with a 100 mΩ resistance, R, and two multimeters[2] (see Figure 4.1). One multimeter measures the voltage drop across the PSC. The other multimeter measures the voltage drop across the resistor and the flowing current I is then calculated using Ohm's law:

$$I = \frac{U}{R}. \tag{4.1}$$

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[1]Kukusuki
[2]Keithley 2000 Multimeter

The surface of the holder is structured with rills and connected to a vacuum pump, fixing the PSC on the holder by a vacuum, ensuring mechanical- and electrical contact stability throughout the measurement.

This setup enables safe contact of the probes inside the enclosure and enables reliable EL measurements.

4.3 Luminescence detection

In the setup a CCD camera is used to detect the emitted electroluminescence. The camera detects radiation over a wide range of wavelengths, while the perovskite emits luminescence only at a relatively short range of wavelengths. Therefore, filters are used to detect only EL radiation. Optics focus the emitted radiation at a specific distance onto the imaging sensor. This chapter explains the used components and physical processes.

4.3.1 Filters

Between probe and sensor two low pass filters[3] are used to filter the wavelengths reaching the detector. In filters absorption or interference are used to either transmit or reflect specific wavelengths. The filters in the setup are chosen accordingly to the luminescence emission spectrum of the PSC (see Figure 4.3). This limits the detection of wavelengths to above 718 nm, while limiting the detection of stray light with shorter wavelengths. The filters are part of the photoluminescence capability of the setup, where light emitting diodes (LEDs) optically generate charges in the perovskite. To only detect luminescence from the perovskite, both filters block light emitted by the LEDs.

4.3.2 Optics

Optics focus the radiation onto a charge coupled sensor (CCD). This setup uses a lens[4] with a focus length of 25 mm and an aperature of 1.4, as listed by the manufacturer. The lens is positioned at the minimal object distance of 25 cm away from the PSC. A extender [5] is mounted directly between camera and lens, with a C-mount, doubling the resultion, however decreasing the intensity reaching the camera.
SKETCH FOR LENS SYSTEM

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[3]LP714, LP718
[4]Pentax, C2514-M (KP)
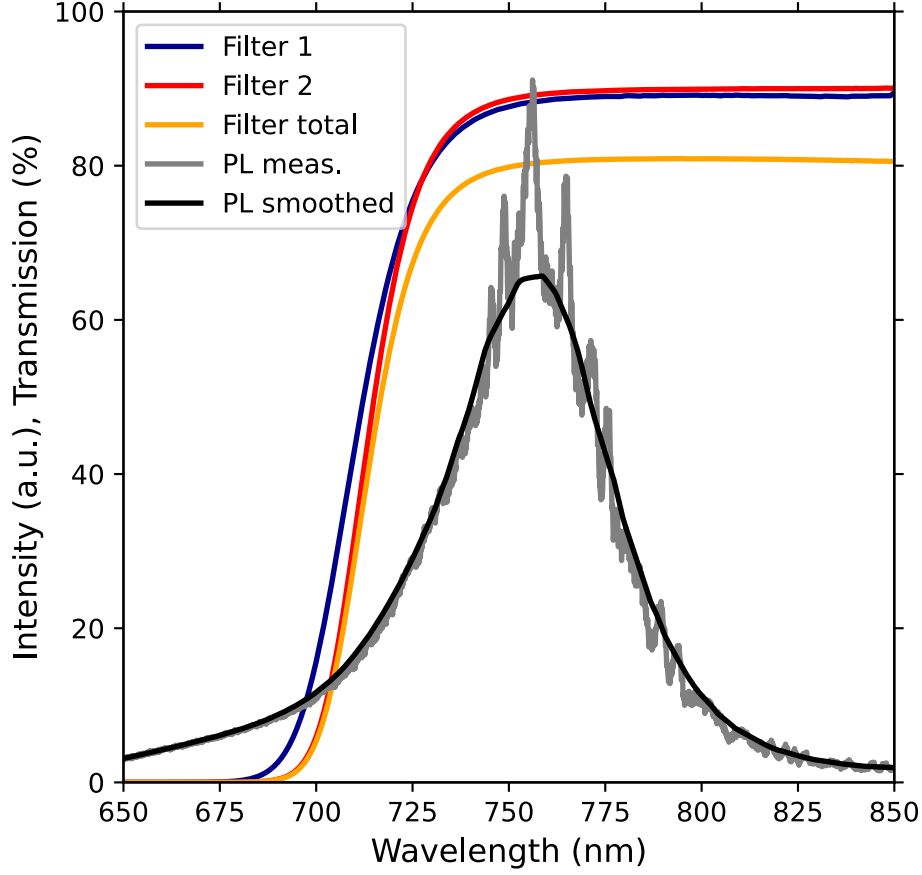[5]Brennweitenverdoppler C - Mount 2-EX / FP-EX2

Figure 4.3: Emitted luminescence spectrum of the perovskite and transmission function of both filters.

4.3.3 Charge Coupled Detectors

The radiation is focused onto a charge coupled device (CCD) image sensor[6] in a camera[7]. CCD sensors are silicon chips structured into small squares, called wells [2](see Figure 4.4). The number of wells correspond to the number of pixel in the taken picture. Radiation generates charges, electrons and holes, and externally applied voltages seperate and trap the charges in the wells. For a specific duration, called exposure time, radiation hits the sensor and charges accumulate in the wells. The amount of generated electrons per incoming photon is called the quantum efficiency (QE), and depends on the sensor material and energy of the photon. The QE for the chosen sensor peaks at 500 nm and decays for larger wavelengths (compare Figure 4.5). For the wavelengths transmitted by the filter (see Figure 4.3), the QE drops to about 10 %, which limits the sensitivity. After the exposure time a series of voltages is applied to shift the charges from the light sensitive wells to opaque covered wells. Then the charges are extracted row by row and the voltage of each well is measured. An A/D converter convertes the voltage into a digital signal, which is

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[6]Sony ICX285-AL
[7]PCO, sensicam qe

saved and later processed. Optical fibers connect the camera to a computer and the software LabView processes the acquired pictures. The software enables automatic control of the setup and acquisition of multiple images with different settings in a row.
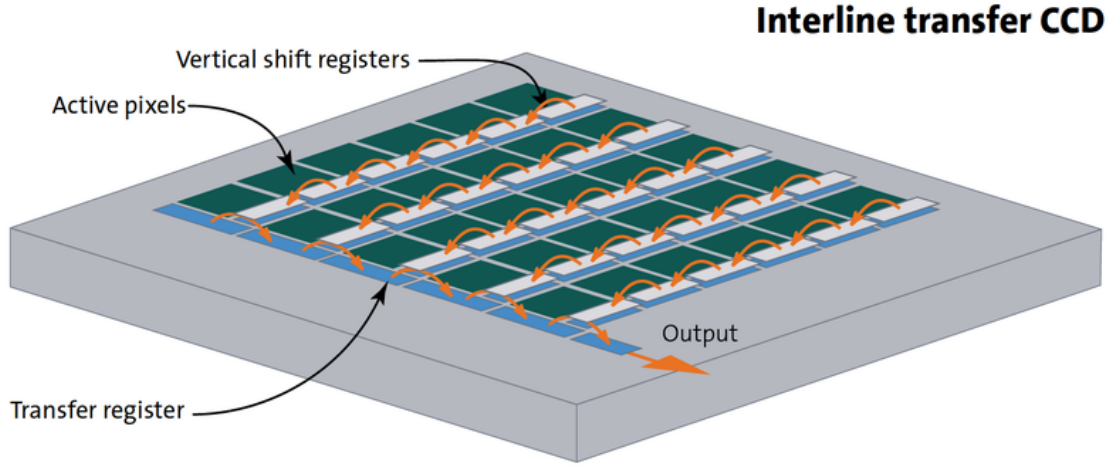

Figure 4.4: Schematic represantation of a CCD sensor. Radiation generates charges in the active pixels and is transferred through vertical shift registers to the transfer register. Taken from [1].

This process measures the EL distribution over the PSC surface. However, several sources of errors occur, which are discussed in the next section.
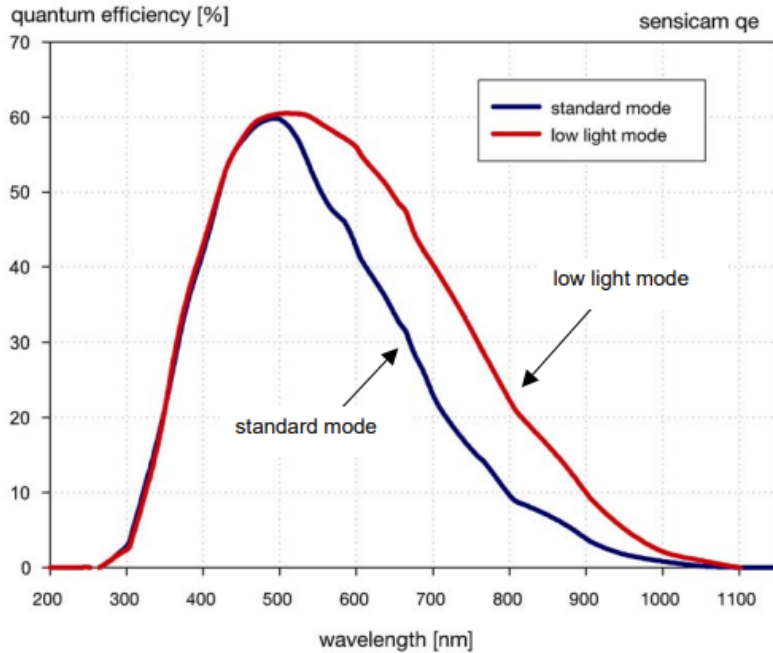

Figure 4.5: Quantum efficiency of the PCO sensicam qe [3].

4.4 Noise and measurement errors

Several sources of errors deviate the measured signal from the physical value. Common errors in the camera image acquisition are dark noise, readout noise and hot or cold pixel (see Table 4.1). Dark noise refers to the thermal generation of electrons, depending on the temperature and the material's properties. To reduce thermal generation the CCD sensor is cooled to -12 °C. To further reduce dark noise, images without illumination or applied voltage are taken, and subtracted from the EL image. Readout noise occurs, when the electrons are shifted from well to well. The manufacturer specifies a read out noise of 5 electrons. This relates to about two counts, with an analog to digital conversion efficiency of 2 electrons per count [3]. EL images are taken at around 3000 counts, 75 % of possible 4096 counts, showing that readout noise can in most cases be neglected.

Furthermore the manufacturer specifies a maximum of two pixels are hot pixels, showing more than 5 electrons. These pixels show increased charge generation in the dark and thus generate a wrong signal, especially at low light intensities. This pixels can be corrected by dark image correction.

Table 4.1: Overview of the characteristic data for the sensicam qe. Specified by the manufacturer [3].

	Sensicam qe
Number of pixels	1376 x 1040
Pixel Size	6.45 μm x 6.45 μm
CCD Temperature	-12 °C
Full Well Capacity	18000 e$^-$
Readout Noise	4...5 e$^-$
A/D Conversion Factor	2 e$^-$/count
Average Dark Charge	< 0.1 e$^-$/pixel sec
Warm Pixels > 5e$^-$	0...2
Delay sensicam LONG EXPOSURE	1 ms ... 1000 s

5 Experimental part

This chapter presents the experimental results of EL measurements on PSCs. Observed were the qualitative interpretation of perovskites, transient behaviour and the localization of defects in different materials of the PSC.

Bibliography

[1]   *CCD Sensor types*. Stemmer Imaging AG. URL: https://www.stemmer-imaging.com/en/knowledge-base/ccd/.

[2]   Gerhard Schnell. *Sensoren in der Automatisierungstechnik*. Vieweg Verlag, 1993.

[3]   *Sensicam Operating Instructions*. PCO. 2004.