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):

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

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

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

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):

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

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).

2.3 Quantum theoretical theory for the absorption and emission of light

[1] BEGIN WITH VECTOR POTENTIAL

The quantum theoretical treatment of light emission or absorption starts with the interaction of electrons with electromagnetic radiation, described by the Schrodinger Equation

$$H\Psi = E\Psi \tag{2.4}$$

with the Wavefunction Ψ, Eigenenergy E and Hamiltonian H(SOURCE):

$$H = \frac{(p + eA)^2}{2m} + V. \tag{2.5}$$

Neglecting terms of order $(eA)^2$, the Hamiltonian can be seperated into the unperturbed part H_0 and the electromagnetic interaction part:

$$H = H_0 + H_i = H_0 + \frac{(eA)^2}{2m} \tag{2.6}$$

and H_0:

$$H_0 = \frac{p^2}{2m} + V. \tag{2.7}$$

In crystals the potential is periodic in space and energy bands are formed, consisting of allowed states and energy gaps . The solution to the unperturbed Hamiltonian H_0 can be calculated approximately by ... and confirmed by experimental techniques (UPS, ...)(PICTURE). That way the Energies E_0 are known and the solution to the perturbed hamiltonian Equation 2.6 can be approximated by perturbation theory (SOURCE). This leads to interaction terms, mixing different states and allowing transisitions obeing transistion rules. First order perturbation theory gives a transition propability from the initial state $|i\rangle$ to final state $|f\rangle$:

$$P_{i \to f} = \frac{2\pi}{\hbar} |\langle f| H_i |i\rangle|^2 \delta(E_f - E_i \mp \hbar\omega). \tag{2.8}$$

Inserting Equation 2.6 yields

$$P_{i \to f} = \frac{2\pi}{hbar} \left(\frac{eA}{mc}\right)^2 |\vec{e} M_{fi}(\vec{k})|^2 \delta(E_f - E_i \mp \hbar\omega), \tag{2.9}$$

with $M_{fi}(\vec{k})$ being the matrix dipolemoment for states f and i:

$$\vec{e} M_{fi}(\vec{k}) = \langle f| \vec{e}\vec{p} |i\rangle = e \int \overline{\Psi_f}(-i\hbar\nabla)\Psi_i \, d\vec{r}. \tag{2.10}$$

To account for all possible transisitions one has to integrate over all possible values $\vec{k}$ and summing over all initial and final states, denoted by valence band v and

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[1]BassaniPastoriParravicini-ElectronicStatesandOpticalTransitionsinSolidsPergamonPress1975

conduction band c:

$$W(\hbar w) = \frac{2\pi}{\hbar} \left(\frac{eA}{mc}\right)^2 \sum_{v,c} \int \frac{2d\vec{k}}{(2\pi)^3} |\vec{e}M_{fi}(\vec{k})|^2 \delta(E_f - E_i \mp \hbar\omega). \tag{2.11}$$

Returning to the connection between transition propability and absorption coefficient α, which is defined as the ratio of absorbed energy in unit time and unit volume to incoming energy flux:

$$\alpha(\hbar w) = \frac{\text{energy absorbed in unit time and unit volume}}{\text{Energy flux}}. \tag{2.12}$$

The absorbed energy is the photon energy times the total transition rate $W(\hbar w)$. The incoming energy flux is calculated by the Poynting vector from vector field $\vec{A}$. This yields for α:

$$\alpha(\hbar w) = \frac{\hbar c \, 2\pi}{A_0^2 \, wn} \, W(\hbar w). \tag{2.13}$$

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 (EL) measurements. Successful EL measurements consist of charge injection, charge recombination and luminescence detection. Therefore section 4.1 explaines the general setup. The following section 4.2 explains the Perovskite Cell layout and electrical contacting of the cells. The emitted radiation is detected by a camera with the use of additional optics, explained in section 4.3. The chapter concludes with the consideration of noise and 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 oustide, providing further utility. Inside the enclosure are the probe holder and camera. To position the camera according to the sample size and used optics, the camera can be moved in three dimensions.
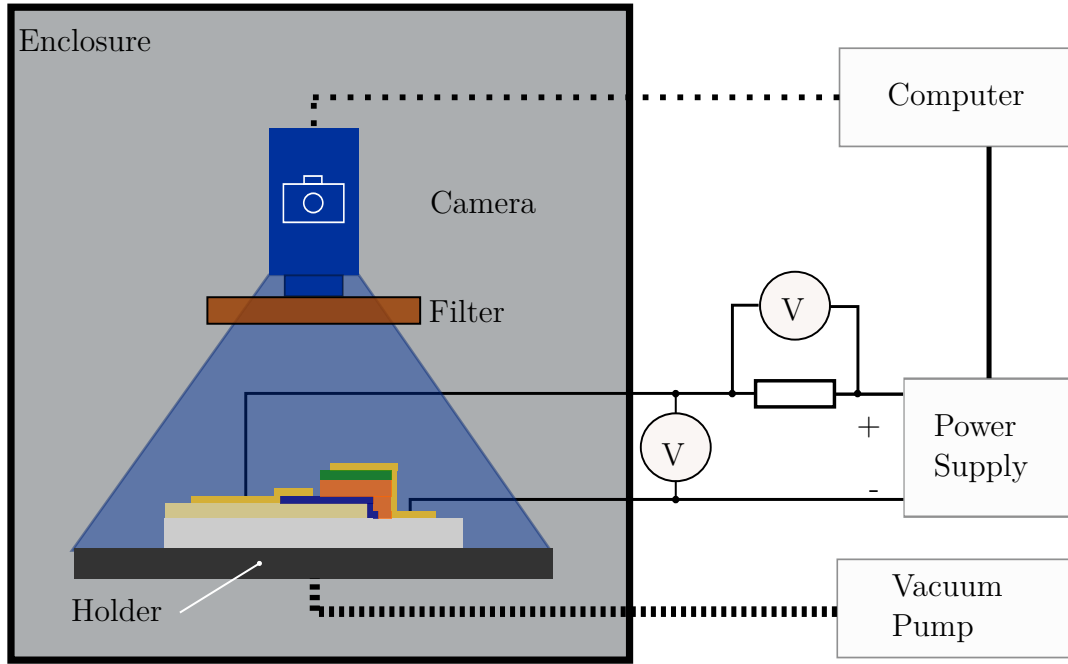
Figure 4.1: Schematic of the EL measurement setup. Camera and Probe are positioned inside the setup, and the computer, power supplies and measurement devices are provided from the outside. Two multimeters are used to measure the voltage drop and current sourced.

4.2 Electrical Connection

Perovskite Solar Cells (PSCs) are manufactured on 25 mm x25 mm glass substrates (see Figure 4.2). Four cells are deposited on one substrate, each single cell having dimensions of 4 mm x 3.5 mm. The cell stack consists of a glass substrate, with a xyz nm thick layer of Indium Tin Oxide (short ITO) deposited ontop. xyz nm of Spiro-TTB are used as a Hole Transport Layer (HTL), followed by 500 nm of methylammonium lead triiodide (short MAPI) as the absorbing layer. The top side of the MAPI is contacted with xyz nm of C60 and BCP, acting as the Electron Transport Layer (short ETL). In the end of the fabrication process, xyz nm Gold are deposited on top of the ITO and the C60/BCP. To succesfully contact the PSC a holder with four pins is used. The holder uses two pins to check proper contacting of the PSC and the other two to source voltage.

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). The 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 by Ohm's law:

$$I = \frac{U}{R}.$$
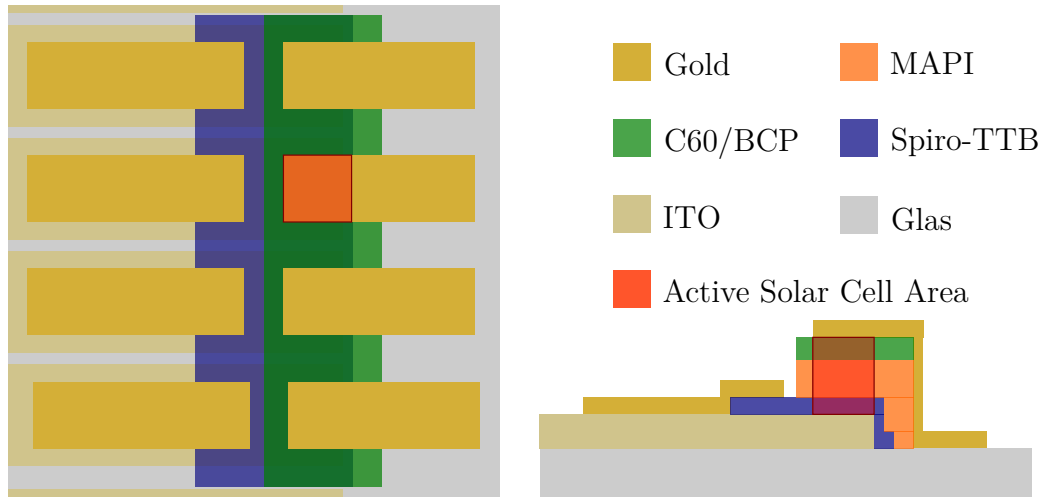
(4.1)

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[1]Kukusuki
[2]Keithley 2000 Multimeter

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

Structured wells with a vacuum connection fixate the PSC on the holder. This ensures mechanical and electrical contact stability throughout the measurement.

This setup enables safe contacting of the probes inside the enclosure. After correct poling, charges are injected and recombine. The emitted radiation is detected by a camera, what requires the usage of filters and optics.

4.3 Luminescence detection

In the setup a ccd camera detects the emitted luminescence. The camera detects radiation over a wide range of wavelengths, while the perovskite emits luminescence only at specific wavelengths with small halbwertsbreite. Therefore filters are used to detect only the 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 a filter[3] is used to filter the wavelengths reaching the detector. In filters absorption or interference are used to either transmit or reflect specific wavelengths. The filter in the setup is a bandpass filter and chosen accordingly to the luminescence emission spectrum of the PSC (see Figure 4.3). This reduces the detected wavelengths to 780 nm to 800 nm, the interval with maximal intensity of the PSC, which enables maximum sensitivity to the emitted radiation and limits the detection of stray light.

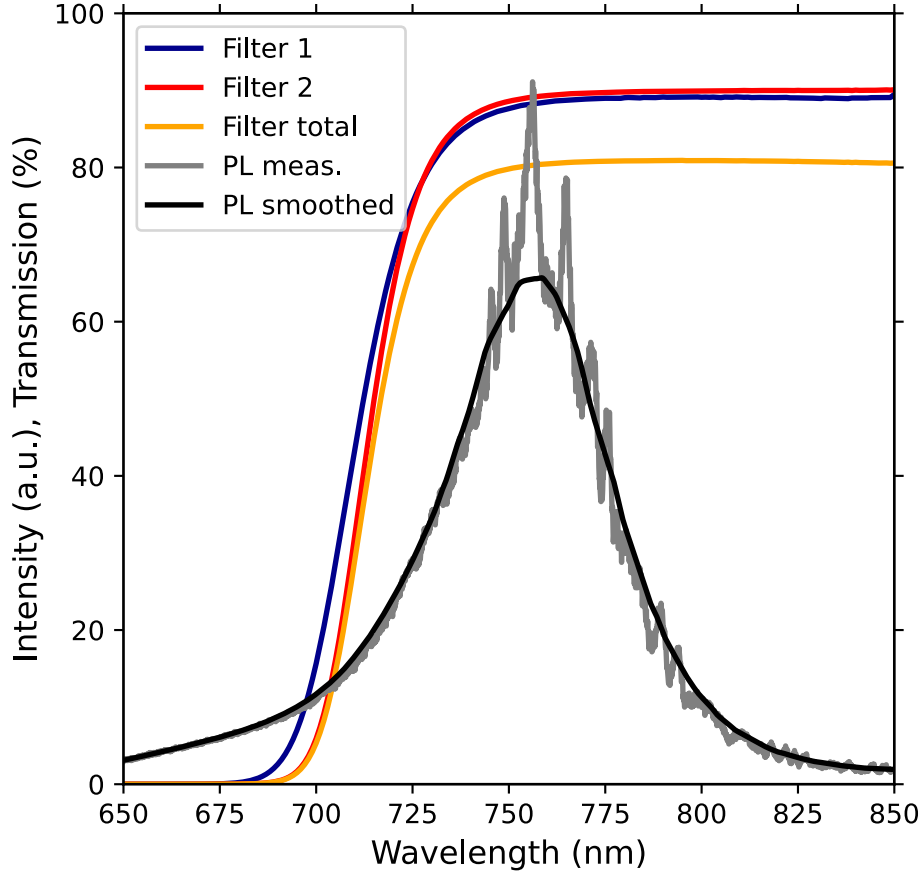[3]bk-Interferenzoptik, custom made product

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

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 and mounted directly to the camera with a C-mount.
SKETCH FOR LENS SYSTEM

4.3.3 Charge Coupled Detectors

The radiation is focused onto a charge coupled detector (CCD) sensor[5] in a camera[6]. CCD sensors are silicon chips structured into small squares, called wells [**SchnellCCD1993**](see Figure 4.4). The number of wells correspond to the number

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[4]Pentax, C2514-M (KP)
[5]Sony ICX285-AL
[6]PCO, sensicam qe

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 time, 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 **??**). For the wavelengths transmitted by the filter (see section before), the QE deops to about 10 %, which reduces 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 an digital signal, which is saved and later processed.

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

4.4 Noise and measurement errors

Several sources of errors deviate the measured signal from the physical value. Common errors are dark noise, readout noise and hot or cold pixel. 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.

Other sources of errors happen when the electrons are shifted from well to well,
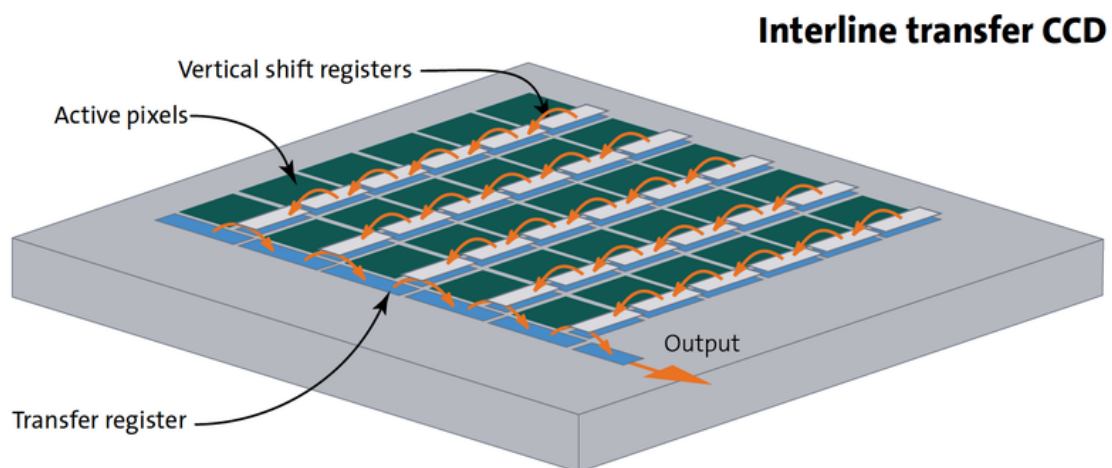

Figure 4.4: Schematic represantation of a CCD sensor. Radiation generates charges in the active pixels and is transferred through vertical shift registers to the transfer register. Taken from [**StemmerCCD**].

called readout noise. The manufactur specifies the read out noise of 5 electrons. This relates to about one count, with an analog to digital conversion efficiency of 4 electrons per count.[**ManualSensicam**]

5 Experimental part

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