

Master in Photonics

MASTER THESIS WORK

**EXPERIMENTAL SETUP FOR CARRIER LIFETIME
MEASUREMENT BASED ON PHOTOLUMINESCENCE
RESPONSE**

Luis Nogueira Vázquez

Supervised by Dr. Isidro Martín (UPC)

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Experimental setup for carrier lifetime measurement based on photoluminescence response. Design, construction and calibration.

Luis Nogueira Vázquez

Grup de Recerca en Micro i Nanotecnologies, Departament d'Enginyeria Electrònica, Universitat Politècnica de Catalunya, Edifici C4, Campus Nord, C/Jordi Girona 1-3, 08034 Barcelona, Spain

E-mail: luizz_nogueira@yahoo.es

Abstract. The measurement of the effective carrier lifetime in silicon has a great importance for material characterization in the photovoltaic field since carrier lifetime represents a fundamental quality factor in solar cell production. Photoluminescence is a technique that allows lifetime measurement at low injection level not affected by the measurement artifacts (minority carrier trapping and the depletion-region modulation) typically found in other techniques.

We have designed and constructed a device to calibrate and measure the photoluminescence response of silicon solar cells. Then we have applied the quasi-steady-state photoluminescence technique (QSS-PL) to obtain the minority carrier lifetime curve. The objective is to extend the available measurement range to obtain additional information about surface recombination.

Keywords: Solar cell, Photoluminescence, Surface Recombination, Carrier Lifetime.

1. Introduction

Nowadays the energy production is based in a large percentage on fossil fuels. Two factors are making us change this market structure: the shortage of fuels and the environmental problems derived from the gas emissions which contribute to the climate change.

In this context, the photovoltaic conversion of the solar energy is expected to develop an important role replacing the existing energy production. Several studies suggest that there will be a huge increment of the photovoltaic market in the near future and specially in the period 2020-2040 [1]. Figure 1 shows the evolution of the photovoltaic energy production in the world in megawatts peak (MWp) produced annually. As it can be seen, there is a very important upward trend in absolute and percentage terms.

To progress in the energy market and not depend on public bonus it is necessary to reduce the costs of the photovoltaic solar energy and improve or maintain the efficiency. Currently the cost-energy relationship is around 2-3 €/Wp, while experts have numbered the decrease to be competitive to 0.5 €/Wp or even less [1].

The key to reduce the costs of solar energy production is to reduce the manufacturing costs of the devices, in other words, to reduce the costs of solar cells. The main technologies in solar cells are based on silicon (organic cells and other possibilities are under study), so the efforts should be focused on reducing the costs of silicon solar cells.

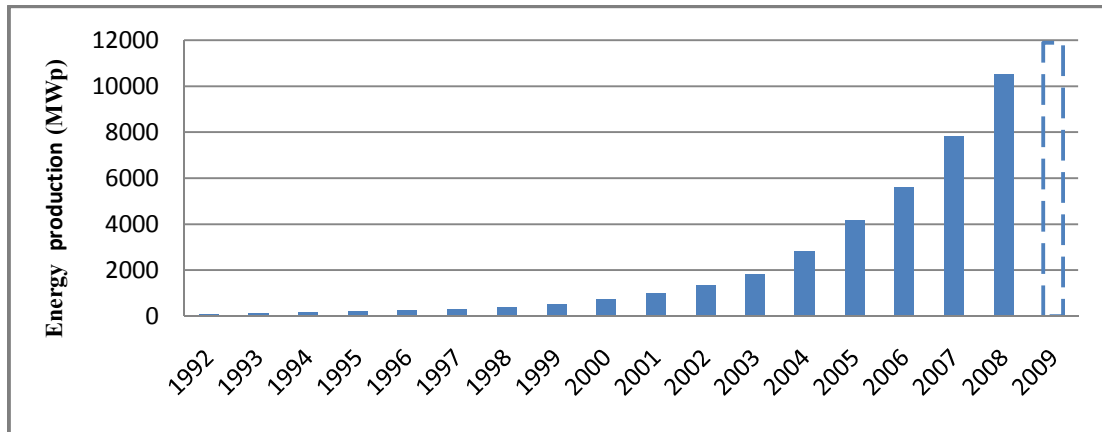


Figure 1: Annual evolution of the solar energy production in megawatts peak.

It is calculated that the 30-50% of the price of a solar cell comes from the initial material, the silicon [2]. Therefore, any reduction of the material costs will be determinant in the final price. The manufacturers have already noticed this, so one of their first strategies has been the rise of the multi-crystalline silicon (mc-Si). This material consists in an agglomerate of small silicon crystals of about some square centimetres, despite having less efficiency it is much more cheaper than the mono-crystalline silicon (c-Si).

Another strategy to reduce the module fabrication costs is to make the silicon wafers thinner. From the 350-400 μm in the past, today the wafer thickness is around 225-250 μm , and it is expected a larger reduction in the short-term with the thin-film technologies. The reduction of the wafer thickness makes it possible to extract and build a larger number of solar cells from the same silicon ingots, thus reducing the costs.

While the wafers become thinner it is important to know and measure their efficiency during the manufacturing process. The effective lifetime (τ_{eff}) of the photogenerated carriers gives us an idea of the recombination rate, which is the loss of these carriers. The information given by the lifetime measurement is fundamental to develop silicon solar cells. In addition, it will be more important to control their efficiency due to the increment of the surface/volume relationship (the reduction of the wafer thickness) and the fact that recombination is dominated by surface processes.

The term “lifetime” refers to multiple physical processes, but is commonly used to describe the recombination processes which are defined as the cancellation of an electron-hole pair. So, the lifetime is not a property of the semiconductor but a relationship involving charge carriers and semiconductor properties. As we work with low injection level conditions then we will measure the “minority carrier lifetime”, but this term sometimes is used for higher injection levels too.

Recently different techniques and instruments that allow a reliable measure of the lifetime dependent on the level of photo-generated carriers or the injection level (Δn) have emerged. Among the different possibilities, the photoconductance is the principal method to measure lifetimes, but at low injection level the technique fails because it is sensitive to artifacts such as minority carrier trapping or depletion-region modulation (DRM) and makes an overestimation of the lifetime [3], [4].

The aim of this master thesis work is to develop a measurement system, including the software and the equipment, to obtain a reliable carrier lifetime with the photoluminescence technique at low injection conditions ($\Delta n < N_A$) avoiding the artifacts above mentioned. On section 2 the theoretical concepts are described. Section 3 presents the configuration and the calibration. Finally section 4 presents the quasi-steady-state photoluminescence technique (QSS-PL) and the results obtained.

2. Theoretical concepts

2.1. Bulk recombination

The generation of excess charge carriers in crystalline silicon (electrons and holes) is provided by thermal activity, electrical excitation or light excitation. Opposite to the generation there is the recombination of such carriers, in which the annihilation of electrons and holes is assisted by several mechanisms. It is a goal of solar cell development to minimize all the recombination processes, so that the light generated carriers can contribute to the photocurrent. The net electron-hole recombination rate (U) can be defined as:

$$U = \frac{\Delta n}{\tau} = \frac{\Delta p}{\tau}, \quad (2.1)$$

where τ is the recombination lifetime which characterizes the recombination process and $\Delta n = n - n_0$ is the excess minority carrier density (or injection density) within the bulk, n is the total electron density and n_0 is the electron density at equilibrium. We assume, all along of this work, the same excess concentration of electrons and holes $\Delta n = \Delta p$, i.e. a photon creates one electron-hole pair.

Crystalline silicon bulk presents three independent recombination processes [2], [5]:

$$U_{bulk} = \frac{\Delta n}{\tau_{bulk}} = U_{Rad} + U_{Aug} + U_{SRH} = \frac{\Delta n}{\tau_{Rad}} + \frac{\Delta n}{\tau_{Aug}} + \frac{\Delta n}{\tau_{SRH}}. \quad (2.2)$$

In the **radiative recombination** process (U_{Rad}) a photon is delivered. Since the electron is at the conduction band and the hole is at the valence band, the delivered photon has approximately the band gap energy of the semiconductor material. The recombination rate is proportional to the density of electrons and holes (n and p), since one of each is needed in this process:

$$U_{Rad} = B(np - n_i^2) \cong B \cdot \Delta n \cdot (N_{dop} + \Delta n), \quad (2.3)$$

where N_{dop} is the donor or acceptor density, and n_i the intrinsic carrier density of silicon. In c-Si the radiative constant B has a value of $1 \cdot 10^{-15} \text{ cm}^3/\text{s}$ [6], [7], leading radiative recombination to a negligible rate, i.e. a high lifetime (τ_{Rad}). B has a low value because silicon has an indirect gap and radiative recombination involves 4 particles (two carriers, a photon and a phonon).

In **Auger recombination** (U_{Aug}) the excess energy of the transition is given to another charge carrier. Auger recombination dominates at high injection level.

And in **Shockley Read Hall recombination** (U_{SRH}), the recombination takes place through a defect whose energy level is located within the forbidden energy band gap, the excess energy is delivered by phonons. Both electrons and holes can be trapped. SRH recombination dominates at low injection level.

2.2. Surface recombination

At the semiconductor surface the crystalline network is completely lost and there is a high density of defects within the forbidden energy band gap. Hence the surface recombination rate is described by the SRH theory [8], [9].

We can separate the front and back surface rates of the solar cell [10]:

$$U_s = U_{s,front} + U_{s,back} = S_{eff,front} \cdot \Delta n + S_{eff,back} \cdot \Delta n, \quad (2.4)$$

where S_{eff} is an effective surface recombination velocity ($\text{cm} \cdot \text{s}^{-1}$) and Δn is the minority carrier density at the quasi-neutral bulk, i.e. practically along the whole c-Si wafer thickness. It must be mentioned that very often a space charge region is created at the surfaces and a big

difference can be founded between carrier densities at the surfaces and at the bulk. Since Δn can be easily measured and controlled by changing the illumination level, the surface recombination rate is related to the bulk carrier density instead to the surface density. The impact of the space charge region is then included in S_{eff} .

2.3. Effective lifetime

The Effective lifetime includes any recombination process: $\sum_i U_i = \frac{\Delta n}{\tau_{eff}}$.

Making the following assumptions:

- The y- and z- dimensions of the wafer are much longer than the x- dimension.
- τ_{bulk} is constant within the wafer.
- Both surfaces have the same S_{eff} value: $S_{eff,front} = S_{eff,back}$.
- The photo-generation rate within the wafer (G_{ext}) is constant through the wafer leading to a constant profile of the excess carrier density Δn .

A relationship between τ_{eff} and the bulk and surface parameters can be calculated:

$$\sum_i U_i = \frac{\Delta n}{\tau_{eff}} = \int_{-W/2}^{W/2} U_{bulk} dx + U_{s,front} + U_{s,back} = \frac{\Delta n \cdot W}{\tau_{bulk}} + 2S_{eff} \cdot \Delta n, \quad (2.5)$$

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + 2 \frac{S_{eff}}{W}. \quad (2.6)$$

In order to measure τ_{eff} we use the continuity equation of minority carriers [11]:

$$\frac{d\Delta n}{dt} = G_{ext}(t) - \frac{\Delta n}{\tau_{eff}} - \frac{1}{q} \frac{dJ_n}{dx}, \quad (2.7)$$

where $G_{ext}(t)$ is the generation rate and J_n is the current density of electrons, as we work in open-circuit conditions (the solar cell is not connected) $J_n = 0$.

Therefore, τ_{eff} can be defined as follows [2], [5], [11]:

$$\boxed{\tau_{eff} = \frac{\Delta n}{G_{ext}(t) - \frac{d\Delta n}{dt}}}. \quad (2.8)$$

This equation describes the general behavior of the effective lifetime of a silicon wafer under any illumination source. The lifetime is only dependent on the injection level (Δn) and the external generation rate (G_{ext}). The latter can be easily measured with a calibrated photosensor that measures the light intensity that arrives to the solar cell. On the other hand, in this work we use the photoluminescence response of the semiconductor material to evaluate the radiative recombination rate and, thus, obtain a value for Δn . This is explained in the following section.

3. Photoluminescence. Experimental setup and calibration

Photoluminescence is a process in which the substrate absorbs and re-radiates photons. In a general approach, we use the photoluminescence response for a contactless, nondestructive method of probing the electronic structure of materials useful to measure the effective lifetime.

Light is directed onto a sample, where it is absorbed in a photo-excitation process. The energy can be dissipated by the sample through the reemission of light. Radiative transitions in semiconductors can involve localized defect levels. The photoluminescence energy associated with these levels can also be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration [4], [12].

In our case, we are interested in the radiative process where an electron in the conduction band recombines with a hole at the valence band. Then, the energy of the reemitted light is related to

the band gap energy. At room temperature, silicon has a band gap of 1.12 eV, hence its reemitted light has a wavelength peak at 1140 nm [13], [14]. The quantity of the reemitted light is related to the radiative recombination rate and to Δn through Equation (2.3). We will characterize Δn and, thus, τ_{eff} with the photoluminescence response.

3.1. Experimental setup

Figure 2a presents the block diagram to calibrate the τ_{eff} based on the photoluminescence response of the c-Si wafer [15], [16]. A picture of the whole equipment is given in Figure 2b.

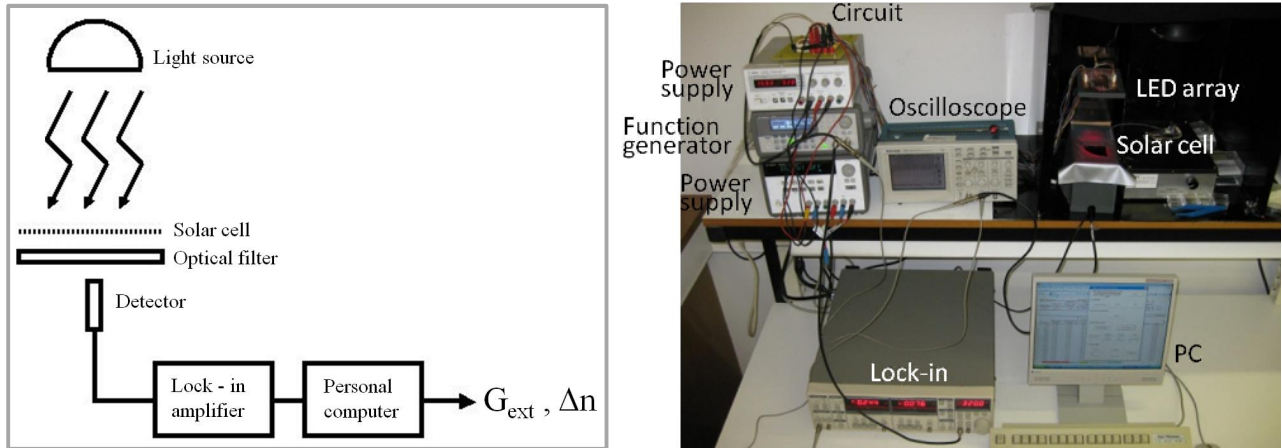


Figure 2: (a) Block diagram of our τ_{eff} calibration system; (b) Image of the whole setting.

The light source is an array of 7 red LEDs with a wavelength of 650nm (the spectral distribution is in Figure 3a). It has a power supply and a function generator connected to the circuit above (Fig. 2b), and then connected to the array of LEDs (Fig. 3b).

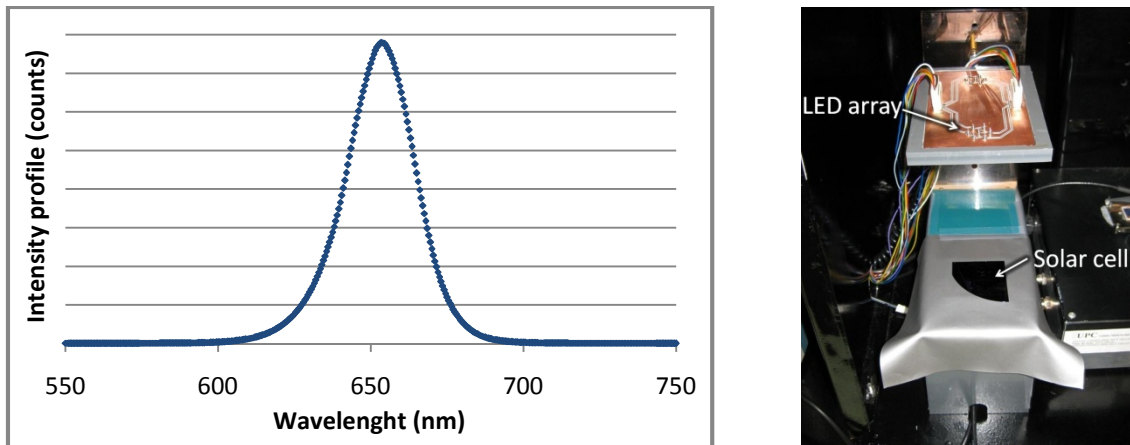


Figure 3: (a) Spectral distribution of the LED's; (b) Top view of the device, the LED array and the solar cell.

The light of the LEDs is focused on the solar cell. The data exposed in this work was obtained with a solar cell of 253 μm thickness and an acceptor density of $N_A = 5 \cdot 10^{15} \text{cm}^{-3}$. The solar cell reflects the 4.8% of the light at 650nm (Fig. 4a), some of the remaining light (95.2%) is absorbed and reemitted over 1140 nm in any direction [13], [14].

On the detector there is an optical filter which attenuates the red light at 650nm and transmits the infrared light over 1140nm (the spectral response of the filter is in Figure 4b). Then the light is detected with the Hamamatsu G6126 infrared detector (Fig.5e), an InGaAs photodiode.

The detector sends a voltage (proportional to the detected light intensity) to the lock-in amplifier (also known as phase-sensitive detector), which measures the real and the imaginary parts of the voltage (the solar cell introduces a phase shift). Finally these values are sent to the

personal computer, via a GPIB, where they are used to calculate the phase and the amplitude of the detected light intensities (I_{PL} and I_G), to obtain Δn and G_{ext} .

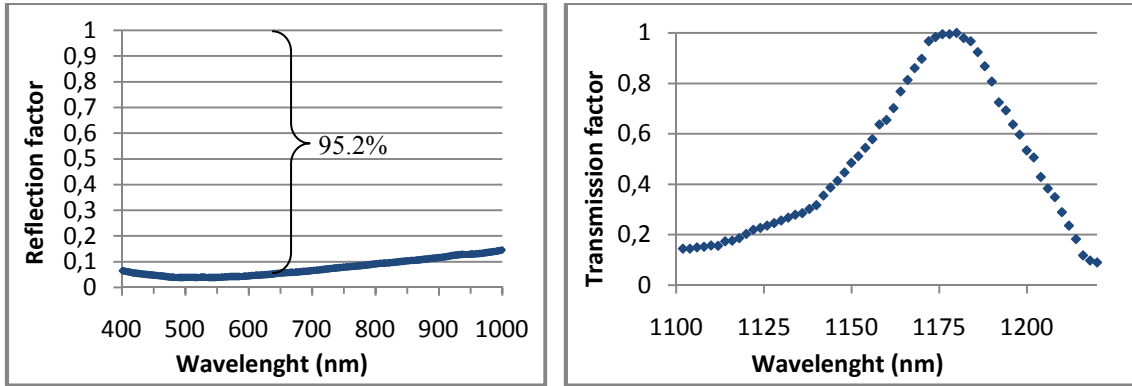


Figure 4: (a) Optical factor of the solar cell; (b) Spectral transmission response of the optical filter.

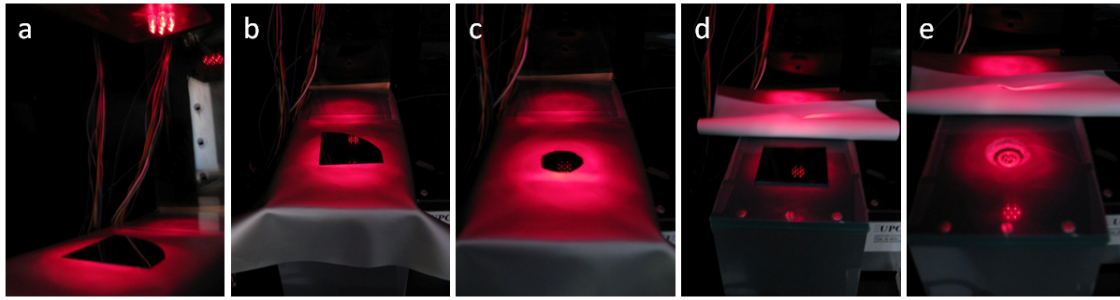


Figure 5. Different images of the device: (a) The Led array and the solar cell; (b) The solar cell; (c) The hole in the "foscurit" material; (d) The filter; (e) The infrared detector.

3.2. Fundamentals of lifetime measurement from photoluminescence response

A constant light intensity is generated using the function generator connected to the LEDs. That is stationary condition:

$$\frac{d\Delta n}{dt} = 0. \quad (3.1)$$

Therefore Equation (2.8) can be simplified to:

$$\tau_{eff} = \frac{\Delta n}{G_{ext}}, \quad (3.2)$$

τ_{eff} only depends on Δn and G_{ext} . Firstly, we focus on how to obtain Δn from the photoluminescence signal. As the light detected (the infrared response of the solar cell) comes from the radiative recombination of the wafer, using Equation (2.3) a relationship between the detected IR light intensity I_{PL} (V) and the injection level Δn (cm^{-3}) can be obtained [17], [18]:

$$I_{PL} = A_i \cdot B \cdot \Delta n \cdot (N_A + \Delta n) = f_{cal} \cdot \Delta n \cdot (N_A + \Delta n), \quad (3.3)$$

where A_i is a proportional constant and we have defined the calibration factor f_{cal} ($V \cdot cm^6$) as $A_i \cdot B$. This quadratic equation can be resolved to obtain Δn :

$$\Delta n = -\frac{N_A}{2} + \sqrt{\frac{N_A^2}{4} + \frac{I_{PL}}{f_{cal}}}. \quad (3.4)$$

On the other hand, to measure the photo-generation rate G_{ext} ($cm^{-3} \cdot s^{-1}$) we need to take out the solar cell and measure the light intensity at 650nm that transmits the filter I_G (V). Some

parameters must be taken into account [19]: the volts/suns conversion factor at the detector ($f_{V/suns} = 1.5 \text{ V} \cdot \text{cm}^2 \cdot \text{suns}^{-1}$), the effective optical transmission factor of the sample at 650nm ($f_{opt} = 0.952$, Fig. 4a) and the thickness of the wafer (W). Applying that the available photons at 1 sun are $46\text{mA}/1.16^{-19}\text{C}$ the expression can be written as follows:

$$G_{ext} = I_G \cdot \frac{f_{opt}}{f_{V/suns}} \cdot \frac{0,046 \text{ C/s}}{W \cdot 1.6^{-19}\text{C}} = I_G \cdot f_G. \quad (3.5)$$

With the Equations (3.4) and (3.5) we can rewrite the Expression (3.2) as follows:

$$\tau_{eff} = \frac{\Delta n}{G_{ext}} = \left(-\frac{N_A}{2} + \sqrt{\frac{N_A^2}{4} + \frac{I_{PL}}{f_{cal}}} \right) / (I_G \cdot f_G), \quad (3.6)$$

The only parameter that we don't know the value is the calibration factor (f_{cal}) that relates the photoluminescence response to Δn . In the following section we propose a method to calibrate it.

3.3. Self-consistent calibration

To determine f_{cal} we add a sinusoidal signal to the constant illumination, this sinusoidal signal has low amplitude (10% of the constant signal) and low frequency. This modulated light is related to a photogeneration rate $G_{ext} = G_0 + G_1 e^{i\omega t}$, where G_0 is the bias illumination, G_1 is the amplitude of the modulated generation and ω is the modulation frequency. Now with the excess carrier density being $\Delta n = \Delta n_0 + \Delta n_1 e^{i\omega t}$ we can define the phase shift φ with respect to G_1 . It can be demonstrated that the frequency response of the semiconductor is described as a low pass filter described by the differential lifetime (τ_{dif}), whose phase shift follows the expression [20]:

$$\tan(\varphi) = -\omega \cdot \tau_{dif} \Rightarrow \tau_{dif} = \tan(-\varphi) / \omega. \quad (3.7)$$

The lock-in allows us to measure only the AC light response of the solar cell: a linear but phased response of the input signal because a solar cell acts as a low-pass filter (Figure 6).

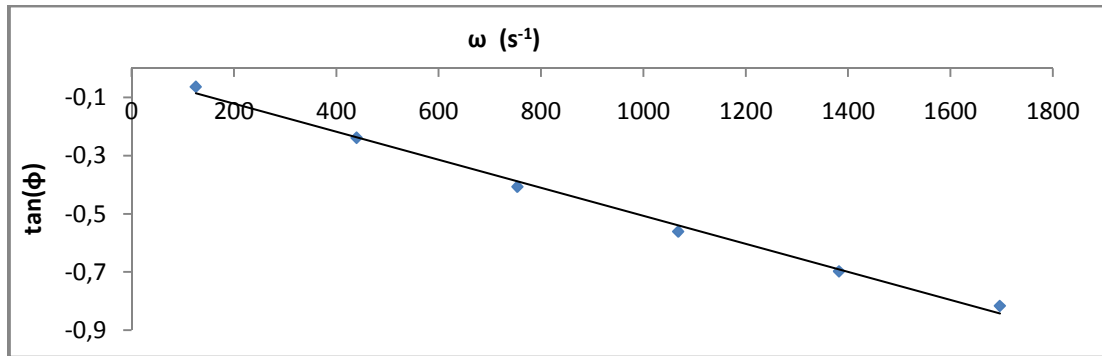


Figure 6: Phase response of the solar cell (a low-pass filter). It is represented the phase ($\tan(\varphi)$) dependent on the angular velocity ($\omega = 2\pi f$).

From the AC measurement of the lock-in we obtain τ_{dif} . On the other hand, the definition of τ_{dif} is the derivative of Δn on G_{ext} i.e. the division of small increments of Δn and G_{ext} [21]:

$$\tau_{dif} = \frac{\delta(\Delta n)}{\delta G_{ext}} = \frac{\Delta n_1}{G_1} = \left(-\frac{N_A}{2} + \sqrt{\frac{N_A^2}{4} + \frac{I_{PL}^{AC}}{f_{cal}}} \right) / (I_G^{AC} \cdot f_G), \quad (3.8)$$

notice that we are using the superscript AC: I_{PL}^{AC} is the module of the AC photoluminescence response and I_G^{AC} is the module of the AC photogeneration intensity.

Therefore we can obtain f_{cal} isolating it in Equation (3.8):

$$f_{cal} = I_{PL}^{AC} / \left[\left(\tau_{dif} \cdot I_G^{AC} \cdot f_G + \frac{N_A}{2} \right)^2 - \frac{N_A^2}{4} \right], \quad (3.9)$$

in our case the result for f_{cal} is $2.84 \cdot 10^{-31} \text{ V} \cdot \text{cm}^6$.

This result of f_{cal} can be applied in Equation (3.6) to obtain the effective lifetime (τ_{eff}). The calibration results for τ_{dif} and τ_{eff} are plotted for different light intensities in Figure 8 with big symbols.

4. Quasi-steady-state photoluminescence (QSS-PL). Results

The QSS-PL technique is useful to measure the τ_{eff} for a wide range of injection levels, taking into account the calibration we have done (f_{cal}) and the parameters we have described.

For the QSS-PL technique we make one change in the setup (Fig. 2a): the lock-in amplifier is replaced by an oscilloscope which sends the voltages measured to the PC via the GPIB. Now it is important to take into account the dark current intensity when we measure and use the intensities I_G and I_{PL} .

There is a change in the illumination, now a triangular signal is generated for the LEDs [17], [19], [22]. To apply the QSS-PL technique we do the same procedure than in the calibration method: we measure the intensity of the infrared response of the wafer (I_{PL}) and then we measure the light intensity taking out the solar cell to obtain the generation of the minority carriers (I_G). The results for I_G and I_{PL} are presented in Figure 7. The photoluminescence response has a higher value because the filter reflects the light of 650nm and transmits the reemitted IR light.

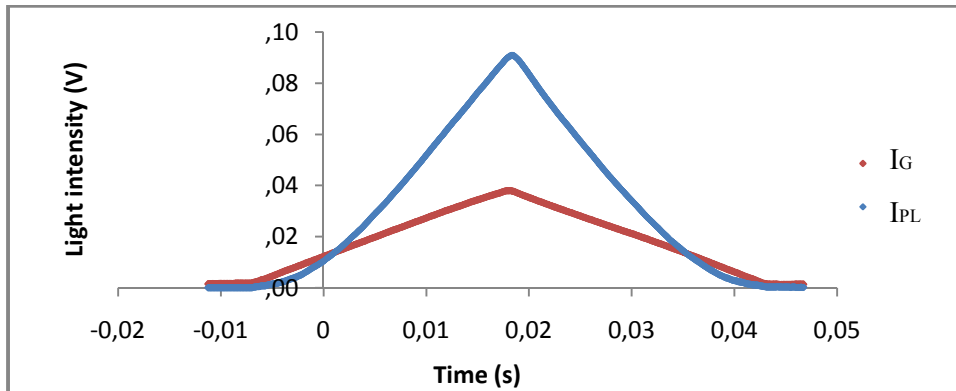


Figure 7: The red light intensity detected taking out the solar cell in red; the infrared photoluminescence response of the wafer in blue.

To obtain τ_{eff} we use Equation (2.8).

- Δn can be calculated from I_{PL} using Equation (3.4) and using the value of f_{cal} obtained in section 3.
- $\frac{d\Delta n}{dt}$ can be extracted from Δn calculating its slope (making linear regressions and deriving).
- G_{ext} can be calculated from I_G using Equation (3.5) and the factor f_G .

Finally we obtain the QSS-PL effective lifetime (τ_{eff}) in the low-injection level. Figure 8 presents the results (τ as a function of Δn in logarithmic scale). It is also represented the QSS-PL differential lifetime (τ_{dif}) and the results obtained during the calibration procedure.

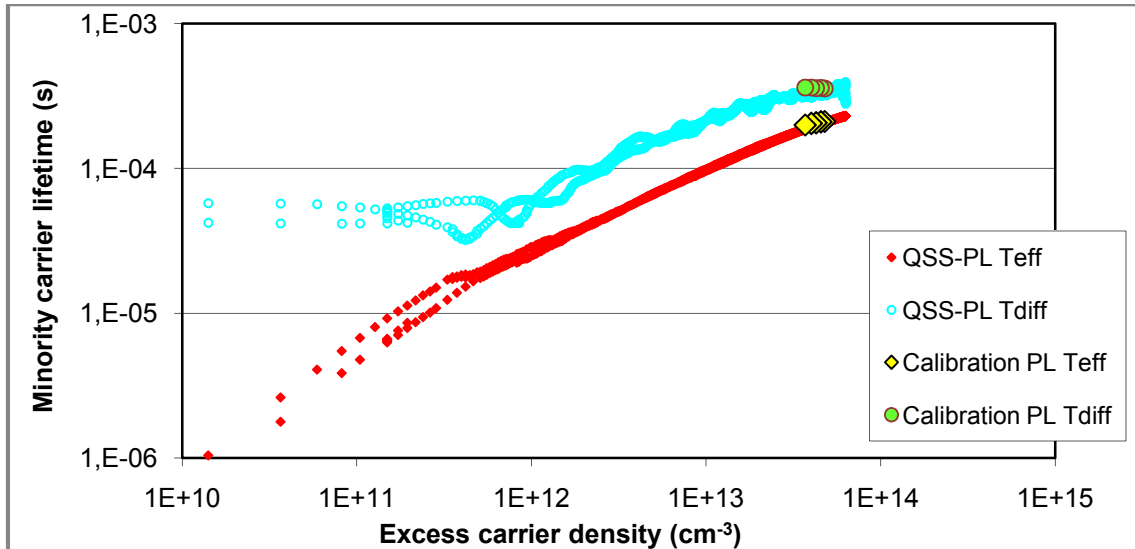


Figure 8: Experimental results for the minority carrier lifetime. The calibration and the QSS-PL.

There are two branches in the curves of the QSS-PL of Figure 8 because we introduce a triangular signal. One branch is related to the ascent and the other branch to the descent of the signal. The two branches overlap, indicating that the calibration has been properly done.

In order to check out if the measurement is properly calibrated, we sent the same sample to the Fraunhofer Institute for Solar Energy Systems (ISE) in Freiburg. This laboratory is considered as the most advanced in the photovoltaic field in Europe and they have developed a QSS-PL set-up with their own calibration procedure, different from the one exposed hereby. Figure 9 presents the comparison of the results obtained at the ISE-Freiburg and the ones measured in this work:

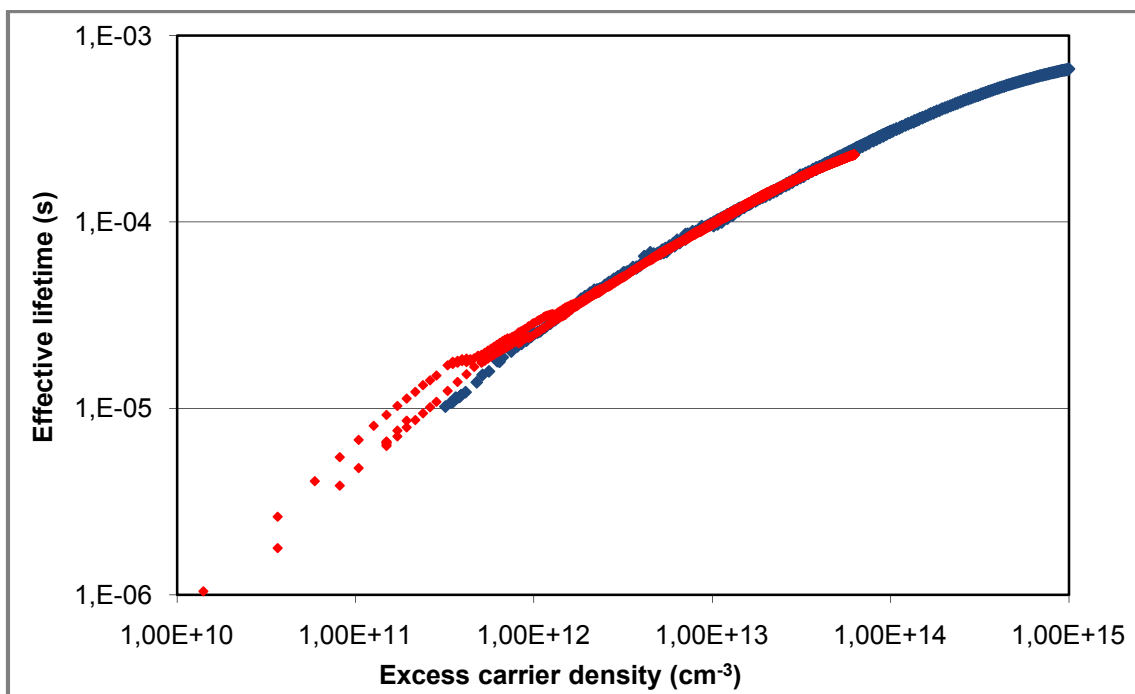


Figure 9: Experimental results for the effective lifetime in red and the ISE results in blue.

As it can be seen, the curves overlap for more than two orders of magnitude. A small difference can be found for very low injection probably related to a higher noise in our set-up. However, this result definitively validates the QSS-PL system designed in this work and its calibration method.

5. Conclusions

We have successfully designed, constructed and calibrated an optical experimental setup to measure the effective lifetime of a solar cell from its photoluminescence response. We have developed the software and the equipment to calibrate and measure the QSS-PL at low-injection level conditions.

Particularly, we propose a new calibration method based on the “small signal” response of the solar cell. All this work has been validate by cross-checking our lifetime data with the ones obtained at ISE-Freiburg.

Acknowledgments

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