

# Diffusion length determination in solar grade silicon by room temperature photoluminescence measurements

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Minority carrier lifetime ( $\tau$ ) and diffusion length ( $L$ ) are the most important electrical parameters to qualify silicon for photovoltaic applications. Amongst the available techniques for measuring this parameter, photoluminescence has regained interest as it can be done on raw material as well as on completed solar cells in a non destructive way. Although very efficient mapping systems can provide fast information on multicrystalline samples most quantitative measurements require a calibration that

is normally achieved by correlation with other techniques like photoconductance decay. In this paper, we show that  $L$  may be evaluated in a simple way from the dependence of the room temperature photoluminescence signal on the excitation beam intensity using an analytical model based on 1D carrier diffusion. Using this 1D model, the diffusion length was calculated in photovoltaic grade silicon materials without calibration by external technique.

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**1 Introduction** Recently, photoluminescence (PL) has regained interest for the characterisation of materials for solar cell applications. Photovoltaic grade multicrystalline silicon (with minority carrier lifetimes below 1  $\mu$ s) and thin Si layers that are used to reduce the cost of the modules require sensitive techniques to determine  $\tau$  or  $L$  values and to characterise the various defects or impurities present in the materials. Fundamental work has already been published on mapping of carrier lifetime obtained from photoluminescence images. M. Tajima has been amongst the first to use PL spectroscopy to measure the doping impurities level in monocrystalline silicon [1]. He was also a pioneer in the field of high resolution PL mapping (down to 1  $\mu$ m) to probe dislocations and related precipitates in silicon [2]. More recently his work has been extended to the study of intra-grain defects in polycrystalline silicon for photovoltaic applications [3]. S. Ostapenko et al. at University of Florida have also published very fundamental results on PL mapping of carrier lifetime in relation with recombination centres in multicrystalline silicon [4]. Many results published since 2000 in the field of photovoltaics are due to T. Trupke et al. at University of New South Wales [5–7]. In particular, they have developed a very fast (a few seconds) and efficient PL imaging technique that allow to

evaluate at room temperature the carrier lifetime distribution, to determine the parallel and series resistance in solar cells and to localise dislocations and impurities. In Europe, several groups are active in the field, like for instance ISE in Freiburg [8] for PL imaging and University of Milan [9] for PL spectroscopy applied to material and process control.

Most of the time, the quantitative determination of carrier lifetime or diffusion length from PL experiments requires a calibration measurement using another technique like Photo-conductance Decay ( $\mu$ W-PCD) or infrared imaging. However, successful approaches have been published where diffusion length was derived from photoluminescence [8] and electroluminescence images [10]. In this paper, we show that the minority carrier diffusion length may be evaluated in a simple way without calibration from the dependence of the room temperature photoluminescence signal on the excitation beam intensity using an analytical model based on 1D carrier diffusion. This approach was first developed to measure the carrier lifetime and the doping density in III-V semiconductor compounds [11]. The objective of this work was to extend the method to various types of silicon that are used for solar cells fabrication.

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tion and to evaluate the limit of applicability of this simple technique. 2D simulations were used to ascertain the validity of the 1D analytical model.

**2 Theoretical approach** At room temperature with above band gap excitation energy, radiative recombination in silicon is mostly due to near band edge transitions. Thus, the PL intensity  $I_{PL}$  is proportional to free carrier densities in both the conduction and the valence bands.

$$I_{PL} = C \beta_r \int_V (n_0 + \Delta n) (p_0 + \Delta p) dV \quad (1)$$

$C$  is a constant related to the fraction of collected PL intensity,  $\beta_r$  is the radiative recombination coefficient of silicon and  $V$  is the luminescence volume. The quantities  $n_0$  and  $p_0$  are the equilibrium carrier concentrations while  $\Delta n$  and  $\Delta p$  are the photo-generated carrier concentrations ( $\Delta n = \Delta p$ ). From Eq. (1),  $I_{PL}$  emitted by a p-type ( $p_0 \gg n_0$ ) material of thickness  $W$  and doping concentration  $N_A$  ( $N_A \sim p_0$ ) after excitation by a circular beam of uniform intensity  $I_0$  with a spot area  $S$  may be expressed as a 1D equation where  $z$  is the distance from the sample surface:

$$I_{PL} = C \beta_r S \left[ \int_0^W N_A \Delta n(z) dz + \int_0^W \Delta n^2(z) dz \right] \quad (2)$$

To obtain Eq. (2), the product  $n_0 p_0 \sim n_i^2$  has been neglected compared to  $\Delta n^2$ . The re-absorption of the luminescence and the lateral diffusion of carriers (supposing a small diffusion lengths compared to the excitation beam diameter) have also been neglected.

The depth distribution of the excess carriers  $\Delta n(z)$  may be calculated by solving the following one dimensional diffusion equation:

$$D_n d^2 \Delta n(z) / dz^2 - \Delta n(z) / \tau + \alpha e^{-\alpha z} (1-R) I_0 = 0 \quad (3)$$

$\alpha$  and  $R$  are respectively the absorption coefficient and the reflectivity of the material at the excitation wavelength,  $D_n$  the diffusion coefficient and  $\tau$  is the bulk minority carrier lifetime. In the following, the bulk lifetime and diffusion length will be used ( $L = (D\tau)^{1/2}$ ). The 3<sup>rd</sup> term of Eq.(3) represents the local electron-hole generation rate. After solving Eq. (3) under appropriate boundary conditions  $I_{PL}$  can be calculated using Eq. (2).

As the excess carrier concentration  $\Delta n(z)$  is proportional to the excitation intensity  $I_0$ , Eq. (2) may be written as a sum of a linear term (low injection) and a quadratic term (high injection):

$$I_{PL} = A I_0 + B I_0^2 \quad (4)$$

General analytical expressions of  $A$  and  $B$  can be found depending on the parameters of the structure [12]. Simplified relationships can be obtained in the case of low recombination velocity at both front and rear surfaces. These conditions can easily be achieved experimentally by surface passivation.

For semi-infinite samples ( $W \gg L$ ) with low recombination velocity at the front surface and small light penetration depth ( $L \gg 1/\alpha$ ),  $I_{PL}$  takes the form:

$$I_{PL} = [C \beta_r N_A L^2 (1-R) / D_n] I_0 + [C \beta_r L^3 (1-R)^2 / 2 S D_n^2] I_0^2 \quad (5)$$

In the case of finite samples with low recombination velocity at both surfaces and small light penetration depth ( $L \gg 1/\alpha$ ),  $I_{PL}$  takes the form:

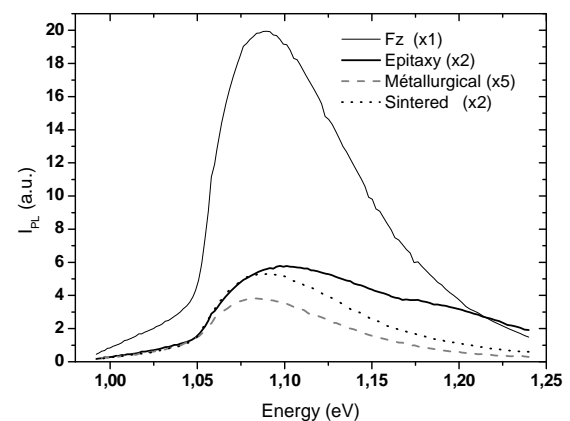
$$I_{PL} = [C \beta_r N_A L^2 (1-R) / D_n] (1 - e^{-\alpha W}) I_0 + [C \beta_r L^4 (1-R)^2 / S W D_n^2] (1 - e^{-\alpha W})^2 I_0^2 \quad (6)$$

Provided the parameters  $R$ ,  $N_A$ ,  $D_n$  and  $S$  can be measured experimentally,  $A$  and  $B$  depends mainly on the carrier diffusion length. It is therefore possible to obtain a theoretical plot of  $B/A$  versus  $L$  from Eq. (7) or Eq. (8):

$$(B/A)_{\text{semi-finite}} = (1-R)L / (2SD_n N_A) \quad (7)$$

$$(B/A)_{\text{finite}} = (1-R)L^2 / (SD_n W N_A) \quad (8)$$

**3 Experimental results and discussion** Various photovoltaic grade silicon substrates were investigated. A high quality FZ monocrystalline wafer was used as a reference. An epitaxial silicon layer with a thickness of 50  $\mu\text{m}$  was deposited on a highly doped substrate [13]. Multicrystalline purified metallurgical silicon and multicrystalline silicon elaborated by sintering of silicon powder were also used in this study. To minimise the non radiative recombination, all samples were passivated on the front surface with an hydrogen-rich silicon nitride layer.

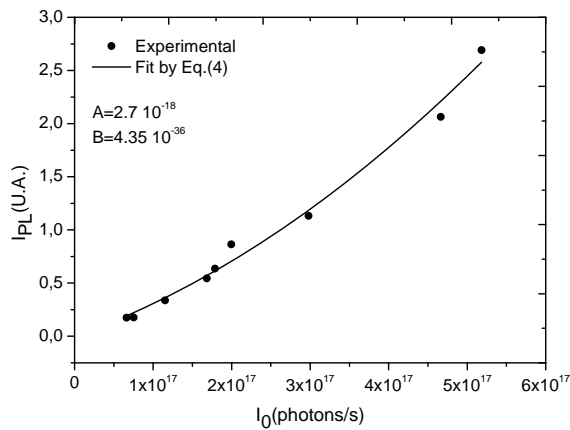


**Figure 1** Room temperature PL spectra from the different samples with a laser excitation power of 200mW. PL intensity was multiplied by the factors in brackets.

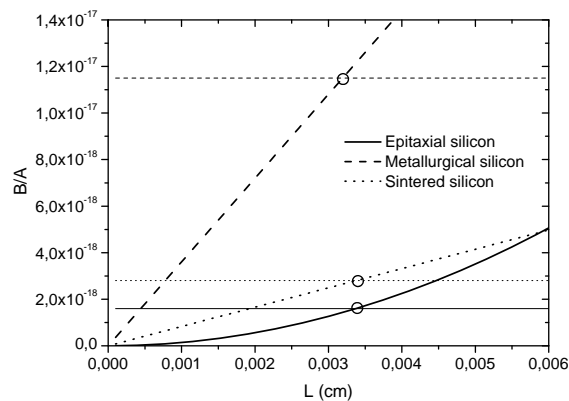
The excitation source was an argon ion laser, emitting at 514.5 nm with a nominal spot diameter of 300  $\mu\text{m}$  at the sample surface and a variable output power up to 1 W. The penetration depth of the excitation beam ( $\alpha^{-1}$ ) was around 1  $\mu\text{m}$  in silicon at the excitation wavelength. The PL signal

was recorded with a highly sensitive nitrogen cooled germanium photodiode and a lock-in amplification technique. Room temperature PL spectra were recorded between 1.24 eV and 0.99 eV with a resolution of 2 nm (Fig. 1). As expected, at room temperature the emission spectrum of silicon consists of a broad band centred around 1.09 eV related to the TO phonon assisted band to band recombination through the band gap.

The integrated intensity of the PL signal was plotted as a function of the excitation power for each sample. The material parameters (diffusion coefficient, doping level and reflectivity) were measured using standard techniques. Experimental  $I_{PL}$  data were fitted according to Eq. (4) to obtain the A and B values and consequently the experimental  $B/A$  ratio (Fig. 2). The diffusion length value was deduced from the intersection of the theoretical curve  $B/A$  with the experimental  $B/A$  ratio as shown in Fig. 3. Equation (8)



**Figure 2** PL intensity  $I_{PL}$  vs. excitation intensity  $I_0$  measured in a metallurgical grade silicon and best fit using Eq. (4).



**Figure 3** Diffusion length  $L_b$  deduced from the intersection of the theoretical plot  $B/A$  (from Eq. (7) or Eq. (8)) with the experimental  $B/A$  ratio.

was used to calculate  $B/A(L)$  for the thin epitaxial layer and Eq. (7) for the other samples. From Fig. 3, the diffusion

length was respectively 34  $\mu\text{m}$  for the thin epitaxial silicon, 32  $\mu\text{m}$  for the metallurgical grade and 34  $\mu\text{m}$  for the sintered silicon. These results are in reasonably good agreement with values measured by Spectral Response (SR) and Light Beam Induced Current (LBIC) [13]. As expected, the model could not be applied to the FZ sample because of its high diffusion length.

To verify the limits of application of the 1D analytical model, numerical simulations with the 2D-DESSIS software were carried out taking into account the lateral diffusion of the generated carriers as well as the dependence on the injection level. 2D-DESSIS simulation was used to simulate the integrated PL intensity by solving the transport equation using a drift-diffusion model and taking into account the various recombination mechanisms depending on the injection level. Table 1 compares the  $L$  values used for the 2D simulation with the values obtained by the analytical 1D method in the case of a simulated sample of thickness 50  $\mu\text{m}$  corresponding to our epitaxial layer. For a given value of  $L$ ,  $I_{PL}$  was calculated as a function of  $I_0$  using 2D-DESSIS software. The theoretical curve  $I_{PL}/I_0$  versus  $I_0$  was fitted by Eq. (4) to deduce a  $B/A$  value. On the other hand the  $B/A$  ratio was plotted as a function of  $L$  using Eq. (8), and a graph similar to Fig. 3, was used to extract the  $L_{1D}$  value. From Table 1, it can be concluded that the 1D model leads to reasonable values of the diffusion length (within 20%) when both surfaces are passivated ( $S_f \approx S_r \leq 100 \text{ cm/s}$ ) and when the spot diameter is larger than the diffusion length.

**Table 1** Comparison between  $L$  values used for the 2D simulation and  $L$  values obtained by the analytical 1D method for the following parameters:  $W=50\mu\text{m}$ ,  $R_s=150\mu\text{m}$  (spot size radius),  $S_f=100 \text{ cm/s}$ ,  $S_r=0 \text{ cm/s}$ ,  $Dn = 26.9 \text{ cm}^2\text{s}^{-1}$ ,  $N_A = 1.5 \times 10^{16} \text{ cm}^{-3}$ .

$B/A^*$	$L (\mu\text{m})^*$	$L_{1D} (\mu\text{m})^{**}$
$2.39 \times 10^{-18}$	10	14
$9.14 \times 10^{-18}$	30	35.5
$1.27 \times 10^{-17}$	40	42.5
$3.84 \times 10^{-17}$	80	76
$4.99 \times 10^{-17}$	100	87.3
$7.92 \times 10^{-17}$	150	/

\*  $L$  used for 2D-DESSIS simulation, \*\*  $L_{1D}$  extracted from the 1D model

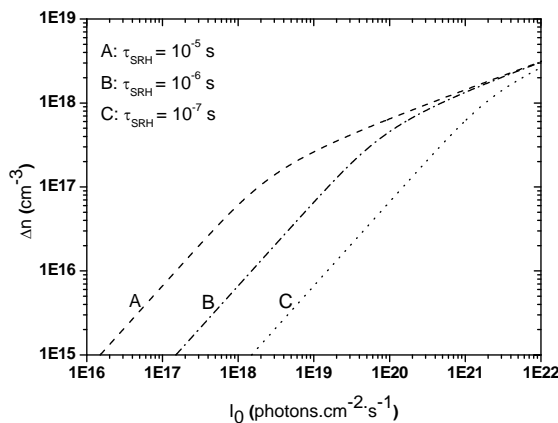
Results have to be analysed carefully with respect to the injection level. From Eq. (4), the PL intensity  $I_{PL}$  undergo a linear (low injection level) and a quadratic (high injection level with  $\Delta n \gg N_A$ ) dependence on the excitation intensity  $I_0$ . It is therefore necessary to estimate the level of photo-generated carriers and compare this number with the doping concentration. The free minority carrier density  $\Delta n$  can be estimated by solving the following equation that links the recombination mechanisms with the generation rate  $G$ :

$$R_{Auger} + R_{radiative} + R_{SRH} - G = 0 \quad (9)$$

Equation (9) can be approximated by [14]:

$$2C_n \Delta n^3 + \beta_r \Delta n^2 + \Delta n / \tau_{SRH} (1-R) \alpha \exp(-\alpha z_p) I_0 / S = 0 \quad (10)$$

where  $C_n$  is the Auger recombination coefficient ( $C_n = 1.1 \times 10^{-30} \text{ cm}^6/\text{s}$ ),  $\beta_r$  is the radiative recombination coefficient ( $\beta_r = 1.1 \times 10^{-14} \text{ cm}^3/\text{s}$ ),  $\alpha$  is the absorption coefficient ( $\alpha \approx 9.4 \times 10^3 \text{ cm}^{-1}$ ) and  $R$  is the reflectivity of silicon with SiN coating ( $R \approx 0.3$ ).  $\tau_{SRH}$  is the excess carriers SRH lifetime that is supposed to be independent of the excess carrier concentration. The generation rate is calculated at  $z_p = 1 \text{ }\mu\text{m}$  below the surface, corresponding to the penetration depth of the excitation light.



**Figure 4** Excess carrier concentration  $\Delta n$  as a function of the excitation intensity  $I_0$  for different minority carrier lifetimes.

Equation (10) can be solved for different values of  $\tau_{SRH}$  as shown in Fig. 4. In our experiments the excitation intensity was in the range  $5 \times 10^{19}$  to  $5 \times 10^{20} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  and the doping levels varied between  $10^{16}$  and  $10^{17} \text{ cm}^{-3}$  approximately depending on the sample (except for the FZ reference substrate). It can be seen that for the  $\tau$  values in the range of  $0.5 \mu\text{s}$  (corresponding to  $L \sim 35 \text{ }\mu\text{m}$ ), the excitation levels used in this work lie rather close to the high injection regime as  $\Delta n$  is of the order of the doping level. However due to detection limit, it was not possible to extend the excitation range towards lower injection level.

**4 Conclusion** In conclusion, a one-dimensional analytical model can be used to evaluate in a simple way the diffusion length of photovoltaic grade silicon samples from room temperature PL measurements. Simulation of PL intensity with 2D software was used to study the limit of validity of the simple analytical model. Furthermore, this technique could be extended to the case of higher purity samples with larger  $L$  or  $\tau$  values by increasing the radius of the excitation spot. A second excitation wavelength could also be added to the experimental set-up to estimate the doping level of the material. PL is therefore a very valuable tool for photovoltaics as it complements other techniques like SR and LBIC when they are not applicable to thin and lower grade materials.

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