

TEMPERATURE-DEPENDENT QUASI-STEADY-STATE PHOTOLUMINESCENCE LIFETIME MEASUREMENTS FOR DEFECT SPECTROSCOPY

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ABSTRACT: Temperature and injection-dependent lifetime measurements of the effective excess carrier lifetime of crystalline silicon enable the determination of characteristic defect parameters like the energetic defect level and the ratio of the capture cross sections of electrons and holes. Since the effect of temperature-dependent photon reabsorption on quasi-steady-state photoluminescence lifetime measurements can be accounted for, this method is well suited to provide data for the spectroscopic analysis of defects in crystalline silicon. In contradiction to other techniques to determine the injection-dependent lifetime like photoconductance measurements, quasi-steady-state photoluminescence stands out for the robustness against parasitic artifacts like depletion region modulation and trapping, which makes it an ideal tool for the purposes of defect spectroscopy. In this work the capability and reproducibility of the determination of defect parameters of titanium contaminated crystalline silicon samples with different doping and defect concentrations will be shown and results will be presented.

Keywords: Photoluminescence, defects, silicon, titanium

1 INTRODUCTION

All measurement techniques to determine the effective excess carrier lifetime τ_{eff} which rely on the sum of the carrier concentrations n_e and n_h for electrons and holes, respectively, are strongly affected by depletion region modulation (DRM) [1] and trapping [2]. These effects lead to an artificially increased τ_{eff} in the low level injection range, as it can be seen in photoconductance-based measurement techniques, like e.g. quasi-steady-state photoconductance (QSS-PC) [3].

Due to the method by evaluating the product of n_e and n_h , quasi-steady-state photoluminescence (QSS-PL) is nearly unaffected against these artifacts [4]. Merely the photoluminescence (PL) signal is affected by trapping processes of the excess carriers proportional to $(n_t + N_{A/D})/N_{A/D}$ with the density of trapped carriers n_t and the doping concentration $N_{A/D}$ of acceptor or donor levels, respectively, which makes PL measurements an ideal technique for lifetime spectroscopy [5] in order to determine the characteristic defect parameters in crystalline silicon.

Since the first measurements of titanium related defect levels could be presented by comparison of temperature- (TDLS) and injection-dependent lifetime spectroscopy (IDLS) [6], the temperature-dependent influence of reabsorption effects turned out to be essential for correct PL spectroscopy and has to be accounted for [7,8]. In order to show the capability and reproducibility of the determination of defect parameters by PL measurements, different titanium-contaminated p-type crystalline float-zone (FZ) silicon samples with varying doping and defect contaminations have been measured and evaluated in this work.

Titanium, a transition metal of the 3d-group of the periodic table of the elements is a component of contact systems in the photovoltaic industry and thus can not be neglected as a potential contamination source of industrially produced silicon solar cells. Due to the relatively low capability of diffusion and solubility, titanium rather tends to form interstitial defect levels than building precipitates [9].

2 THEORY

To determine the effective lifetime of a silicon sample, the excess carrier density Δn has to be extracted from the PL data. In case of a silicon sample with doping concentration $N_{A/D}$, the relative intensity of the PL signal $I_{\text{PL,rel}}$ as the product of the rate of spontaneous emission R_{sp} and a scaling factor A_i can be expressed as

$$I_{\text{PL,rel}} = A_i \cdot R_{\text{sp}} \\ = A_i \cdot B(T, \Delta n) \cdot (N_{A/D} + \Delta n) \cdot \Delta n \quad (1)$$

Hereby $B(T, \Delta n)$ stands for the Einstein coefficient of radiative recombination.

Reabsorption effects can be accounted for by theoretical calculations of the detected photon flux based on the generalized Planck equation [10] and form a calibration correction matrix $\xi_i(T, \tau_{\text{eff}})$, which has to be included in a corrected scaling factor $A_{i,\text{corr}} = A_i \cdot \xi_i(T, \tau_{\text{eff}})$ [7].

The continuity equation under illumination as a function of time is determined by the generation rate G and the total recombination rate

$$\frac{d\Delta n(t)}{dt} = G(t) - \frac{\Delta n(t)}{\tau_{\text{eff}}(\Delta n(t))} \quad (2)$$

assuming homogeneous carrier concentrations. In the latter relationship the recombination rate is expressed in terms of an effective excess carrier lifetime $\tau_{\text{eff}}(\Delta n)$, which itself depends on Δn . The effective lifetime is given as [11]

$$\tau_{\text{eff}} = \frac{\Delta n(t)}{G(t) - \frac{d\Delta n(t)}{dt}} \quad (3)$$

3 EXPERIMENTAL SETUP

In QSS-PL measurements at Fraunhofer ISE and the University of New South Wales, an external monochromatic light source with a wavelength of 810 nm is

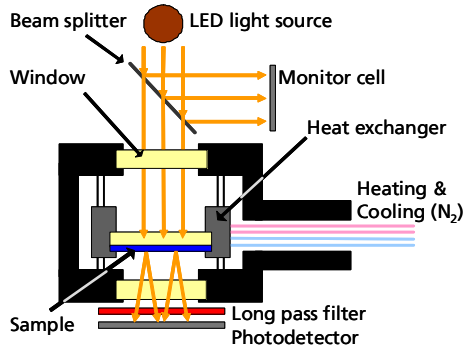


Figure 1: Schematic of the temperature-dependent photoluminescence lifetime measurement setup. The sample is illuminated by a LED light source, generating electron-hole pairs. Some of these recombine radiatively, which can be detected by a silicon photodetector. The generation rate is measured instantaneously by beam splitter and a monitor cell. Latter is calibrated against a reference cell in order to determine the generation rate at all times. The sample is mounted within a cryostatic system, allowing measurement in a temperature range from 77 to 590 K.

used, which illuminates the sample from the front side (see Fig. 1). This light is absorbed within the first few micrometers within the silicon sample by generating electron-hole pairs. A small part of these generated pairs recombine radiatively and thus generate photons with a characteristic energy in the range of the band gap of silicon. By reaching the surface of the sample, emitted photons can be detected by a silicon photodetector at the backside. To avoid parasitic detection of residual photons of the incident light beam, a long pass filter has been placed within the sample and the detection system. The generation rate can be measured instantaneously using a beam splitter and a reference cell.

To measure the effective lifetime within a wide temperature range, a cryostat has been integrated at Fraunhofer ISE in the QSS-PL system. Thus by the use of liquid nitrogen or an integrated heating element, temperatures within 77 – 590 K can be accessed. In order to achieve a certain heat isolation, the cryostat can be evacuated by a vacuum pump down to $< 10^{-6}$ mbar. The thermal conductivity in the vacuum chamber of the cryostat during heating or cooling process was improved by mounting a polished sapphire crystal on top of the sample.

4 MEASUREMENTS

In this work three different intentionally titanium contaminated boron doped $2 \times 2 \text{ cm}^2$ silicon floatzone (FZ) samples with distinctive doping and defect concentrations have been investigated. The samples are passivated with a 70 nm standard silicon-nitride (SiN_x) [12] layer via plasma-enhanced chemical vapor deposition (PECVD) at both surfaces. During crystal growth the contaminant had been added to the melt. Detailed doping- and defect concentrations can be found in Table I. The doping concentration, normally carried out by using a four-point probe sheet resistivity measurement setup or QSS-PC, did not result in reliable

Table I: Characteristic data of the boron doped and with titanium contaminated silicon samples which have been used for this study. During crystal growth, the contaminant had been added to the melt.

	Ti 08	Ti 10	Ti 15
Thickness d (mm)	600	600	600
Doping conc. N_A (cm^{-3})	9.7×10^{14}	1.1×10^{15}	1.7×10^{15}
Defect conc. N_{Ti} (cm^{-3})	4.9×10^{11}	7.0×10^{11}	8.6×10^{10}

results due to an unknown reason. Thus the doping concentrations as determined by the manufacturer were used for subsequent analysis.

The setup has been calibrated at a temperature of 303 K against a QSS-PC [3] measurement. Each sample had been measured initially for calibration at 303 K and in continuation was measured in a temperature range of 78 to 573 K in steps of 15 K. The temperature has been controlled by an integrated heat detector PT 100 located close to the sample.

In Fig. 2 measurement results are shown for sample Ti 08, exemplarily. At a temperature of $T = 303 \text{ K}$ the QSS-PL measurements (left) have been calibrated to a QSS-PC measurement (right). The low level injection (LLI) lifetimes increase from $\tau_{\text{eff}} \sim 2.5 \mu\text{s}$ at 78 K up to $\sim 800 \mu\text{s}$ at 543 K continuously with increasing temperature. Except in the highest measured temperature range the LLI lifetime decreases slightly. This phenomenon is understood very well and can be explained by SRH theory [13,14].

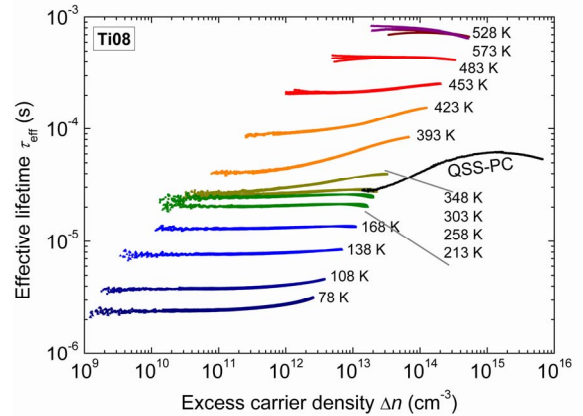


Figure 2: Measurement results shown exemplarily for sample Ti 08. At a temperature of $T = 303 \text{ K}$ the QSS-PL measurements (left) have been calibrated to a QSS-PC measurement (right). For clarity, only selected curves are plotted. The complete measurement consists of injection-dependent measurement curves carried out in a temperature range from 78 K to 573 K in steps of 15 K.

5 LIFETIME SPECTROSCOPY

Defect levels have a significant impact on the effective excess carrier lifetime, which can be explained theoretically by Shockley-Read-Hall (SRH) theory [13,14]. Lifetime spectroscopy of the temperature- and/or injection-dependent LLI-SRH lifetime may allow the determination of characteristic defect parameters.

For TDLS analysis LLI lifetimes were extracted from

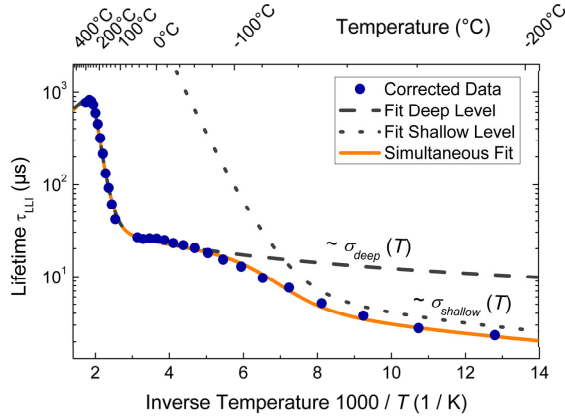


Figure 3: TDLS analysis of measured LLI lifetimes (cf. Fig. 2), exemplarily shown for a titanium contaminated *p*-type silicon sample. The gradient of the Arrhenius-plot behaves proportional to the energetic distance ΔE_i from the band edge to the defect level (left). The second bending (middle) is caused by a second overlapping defect level. A simultaneous fit of both defect levels agrees well with the experimental data. The extracted combinations of the defect parameters ΔE_i , $k(\Delta E_i)$ and the least square deviation $\chi^2(\Delta E_i)$, respectively, have been evaluated in a *defect parameter solution surface* (DPSS), which can be seen in Fig. 5.

the injection-dependent data (cf. Fig. 2) of the three investigated samples and plotted in an Arrhenius-plot, as can be seen exemplarily in Fig. 3. The data can be fitted iteratively by the assumption of two different defect levels in consideration of the model for the temperature-dependent behavior of the capture cross sections $\sigma(T)$. For the analysis of the deep defect level, the defect parameters ($E_C - E_i$) and the symmetry factor $k \equiv \sigma_e/\sigma_h$ as the ratio of the capture cross sections for electrons and holes, respectively, for the additional shallow level were set to fixed values. A least square fit was carried out for the temperature-dependent data for a fixed but gradually varied defect energy depth $(E_C - E_i)^{DPSS}$. Each defect energy belong to a corresponding symmetry factor k^{DPSS} and least square fit error χ^2 . Results can be evaluated in a *defect parameter solution surface* (DPSS) [5], which can be seen in Fig. 5.

As indicated in Fig. 3, the temperature dependence of the capture cross sections have been determined from the low temperature measurement data, which are listed in Table II for all samples.

In order to get additional information about the defect parameters and to specify, whether the TDLS results for the relative defect level ΔE_i belong to the minority-

Table II: The temperature dependences of the capture cross sections $\sigma(T)$ for the deep- and the shallower energy level have to be determined for TDLS analysis [5] (cf. Fig. 3).

	Temperature dependence of capture cross sections $\sigma(T) \sim T^x$	
	χ_{deep}	$\chi_{shallow}$
Ti 08	1.15	1.80
Ti 10	1.45	1.70
Ti 15	1.05	1.60

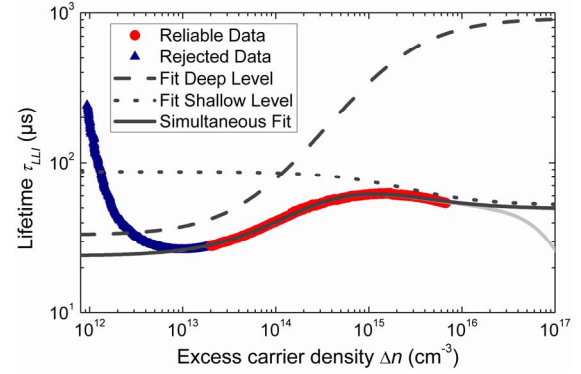


Figure 4: Injection-dependent lifetime spectroscopy (IDLS) – evaluation of the effective excess carrier lifetime τ_{eff} measured by QSS-PC [3]. Below injection densities of $\Delta n \sim 1 \cdot 10^{13} \text{ cm}^{-3}$ data are affected by trapping artifacts and thus have been rejected (blue) for analysis. To fit the reliable data (red) due to SRH-theory, a deep- and a shallower defect level have been assumed.

(MinBH) or majority carrier band half (MajBH), QSS-PC data measured at $T = 303 \text{ K}$ have been evaluated by fitting the injection-dependent behavior of the effective excess carrier lifetime. Results can be seen in Fig. 4, exemplarily. Below injection densities of $\Delta n \sim 1 \cdot 10^{13} \text{ cm}^{-3}$ data are affected by trapping and/or DRM artifacts [1,2] and thus have been rejected for analysis. To fit the reliable data, a deep- and a shallower defect level have been assumed in analogy to the TDLS evaluation. While the deep defect level has a dominating influence in the LLI-range, the influence of the shallower defect level becomes more significant in the high level injection-range. Latter leads to a smooth decrease of the effective lifetime τ_{eff} from $\Delta n \sim 10^{15} \text{ cm}^{-3}$ upwards.

By fitting only one injection-dependent lifetime curve at a defined temperature, no unique result for the existing defect levels within a silicon sample can be extracted. By holding fixed one of the two defect levels for iterative IDLS analysis, for every second defect level $E_C - E_i$ assumed within the silicon band gap, an appropriate symmetry factor $k(E_C - E_i)$ can be found without changing the lowest achieved least square error χ^2 . Thus, an infinite number of solution pairs for $E_C - E_i$ and $k(E_C - E_i)$, respectively, where achieved, which can be seen in Fig. 5. On the other hand a simultaneous IDLS- and TDLS-evaluation complement one another quite well. Thus, comparison of both data sets may lead to determine one solution for $E_C - E_i$.

The evaluation and comparison of TDLS- and IDLS-data of the deep defect level for the samples considered in this work can be seen in Fig. 5. Potential energetic defect levels are indicated by the minima of the least square fit (LSF)-errors. Hereby a tolerable deviation of $2 \cdot \chi^2$ has been considered (Fig. 5, hatched). This leads to deviation boundaries for the energy depth E_i and the symmetry factor k , respectively. The defect levels considered by TDLS in the MinBH (left, respectively) lead to values for χ^2 , which are significantly smaller than the solutions in the MajBH (right, respectively). Thus, the MinBH solution is much more likely.

A comparison with data from the IDLS analysis leads

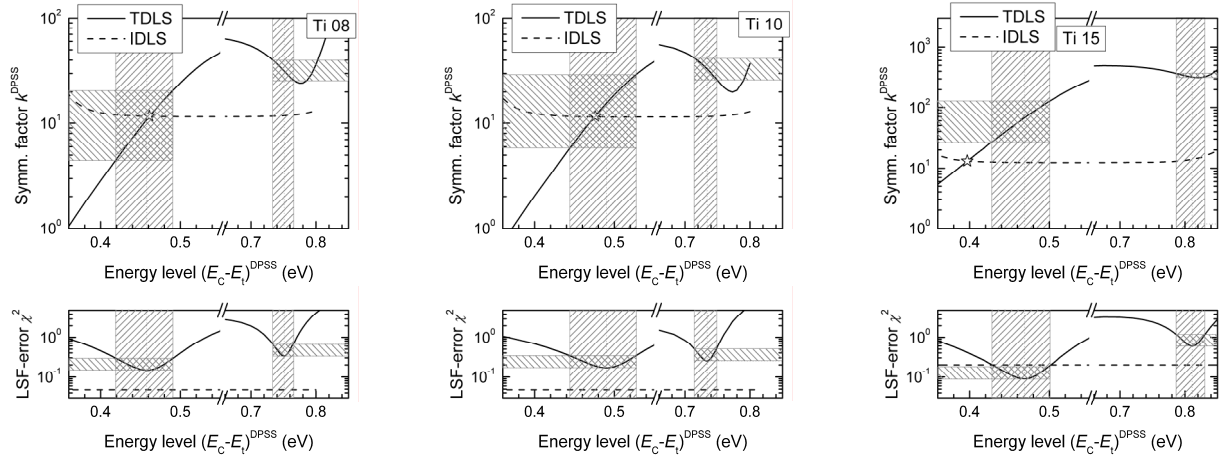


Figure 5: Defect parameter solution surface (DPSS): Evaluation and comparison of TDLS- and IDLS-data of the deep defect level $(E_C - E_t)^{DPSS}$ for the three titanium contaminated *p*-type silicon FZ samples considered in this work. TDLS related data are shown with solid lines while IDLS related data are shown dashed. Potential energetic defect levels follow out the minima of the LSF-errors χ^2 . Hereby a tolerable deviation of $2 \cdot \chi^2$ has been considered (hatched). This leads to deviation boundaries for the symmetry factor k , respectively. The defect levels considered by TDLS in the MinBH (left, respectively) lead to values for χ^2 , which are significantly smaller than the solutions in the MajBH (right, respectively).

to intersections for two of the three samples in the MinBH within the error margins of the TDLS analysis. These intersections of the TDLS and IDLS solution are marked by stars in Fig. 5. On the other hand no intersection could be found for the MajBH solution of TDLS analysis, being another indication that the true defect parameter are the MinBH solution. Thus, the considered deep defect level is consistent to the result achieved in Ref. [8]. Taking the solution of Ti 08 and Ti 10 into account, leads to a weighted arithmetic mean for the deep defect level of $(E_C - E_t)_{deep} = 0.47^{+0.02}_{-0.03}$ eV. The results are shown in Table III.

The evaluation and comparison of TDLS- and IDLS-data of the shallower defect level $(E_C - E_t)_{sh}$ was carried out by the same procedure and can be seen in Fig. 6. In the MinBH (left, respectively) data are consistently afflicted with significantly wider deviation boundaries than in the MajBH. The TDLS analysis of the three

samples shows two distinct minima, one in the MinBH at an energy level of $(E_C - E_t)_{sh,1} = 0.08$ eV, one in the MajBH at an energy level $(E_C - E_t)_{sh,2} = 1.024$ eV. Since the analysis for the MajBH is not sensitive to the symmetry factor k , no values can be determined. The combined analysis of the TDLS and IDLS fits results in different results. While for the Ti 10 sample not enough QSS-PC data at high injection levels were available, the IDLS parameter curves of the samples Ti 08 and Ti 15 intersect with the TDLS parameter curve at an energy level of $E_C - E_t = 0.25$ eV. A possible reason for this discrepancy between the TDLS analysis and the combination of TDLS and IDLS analysis might be different temperature ranges, where the measurement data were taken. While the IDLS data were taken at a temperature of 303 K, for the IDLS analysis temperatures below -50°C were evaluated for the shallow defect level.

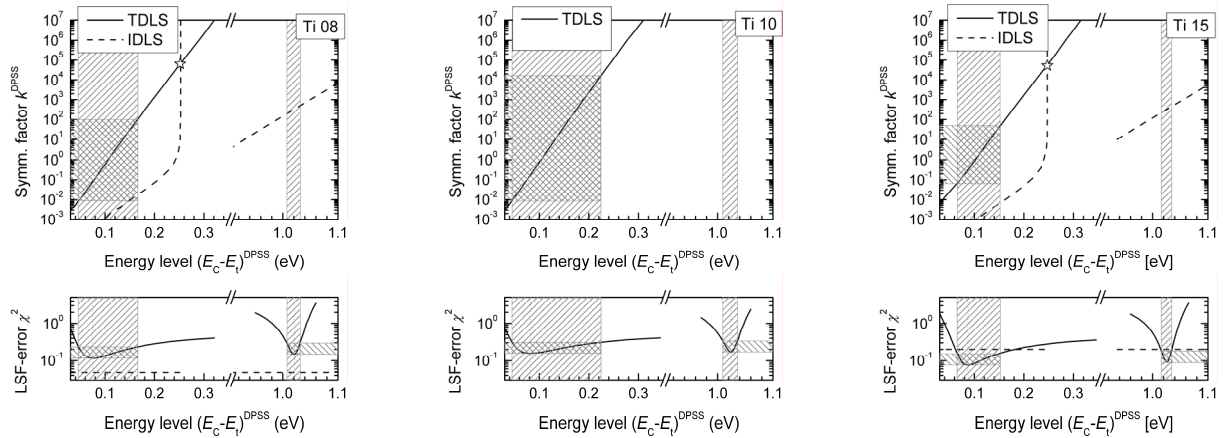


Figure 6: Evaluation and comparison of TDLS- and IDLS-data of the shallower defect level $(E_C - E_t)^{DPSS}$. TDLS-data show two potential results for $(E_C - E_t)_{sh}$, due to quite similar values for χ^2 at the minima, respectively (cf. Table III). In the MinBH (left, respectively) data are consistently afflicted with significantly wider deviation boundaries than in the MajBH.

Table III: Overview of the TDLS measurement results for the deep defect level $(E_C - E_t)_{\text{deep}}$, the corresponding symmetry factors k and the shallower defect level $(E_C - E_t)_{\text{sh}}$, resulting out of the minima of TDLS evaluation and the corresponding LSF-error χ^2 . Due to missing intersection of TDLS and IDLS results, the values set in brackets are not taken into account for building the weighted arithmetic means, respectively. The range for the corresponding k of the shallower defect level can be seen in Fig. 6.

	Ti 08	Ti 10	Ti 15	mean
Deep defect level (eV)				
$(E_C - E_t)_{\text{deep}}$	$0.46^{+0.03}_{-0.04}$	$0.49^{+0.04}_{-0.05}$	$(0.47^{+0.03}_{-0.04})$	$0.47^{+0.02}_{-0.03}$
$k = \sigma_d/\sigma_n$	11^{+10}_{-7}	16^{+14}_{-10}	(70^{+60}_{-40})	13^{+8}_{-6}
Shallow defect level (eV)				
$(E_C - E_t)_{\text{sh},1}$	$0.08^{+0.09}_{-0.03}$	$0.08^{+0.14}_{-0.04}$	$0.09^{+0.06}_{-0.02}$	$0.08^{+0.05}_{-0.02}$
$(E_C - E_t)_{\text{sh},2}$	$1.021^{+0.011}_{-0.013}$	$1.024^{+0.012}_{-0.015}$	$1.026^{+0.008}_{-0.010}$	$1.024^{+0.006}_{-0.007}$

Due to the discrepancy between the TDLS and IDLS parameter curves, only the data of the TDLS analysis are thought to be reliable, with the consequence that no decision based on the TDLS analysis can be done whether the MinBH or the MajBH solution represents the true defect parameters. However, comparing the considered parameters with data from literature, the MinBH solution seems to be much more likely since it perfectly agrees with a shallow defect level found by means of DLTS, being summarized by Ref. [9]. Results considered in this work are summarized in Table III.

5 CONCLUSIONS

Modeling of temperature-dependent low level injection excess carrier lifetime data of three titanium contaminated *p*-type FZ silicon samples resulted in an identification of two distinct defect levels. In combination with an injection-dependent analysis, the defect parameters of the deep defect level could be identified unambiguously to be located in the minority carrier band half of the band gap at an energy depth of $(E_C - E_t)_{\text{deep}} = 0.47^{+0.02}_{-0.03}$ eV with a corresponding symmetry factor of $k = 13^{+8}_{-6}$.

Due to the electron configuration [Ar] 3d² 3s², titanium tends to form interstitial defect levels within the silicon lattice rather than forming precipitates, while the defect levels act mostly donor-like [15]. Also the fact of a symmetry factor $k > 1$ indicates a probable donor-like behavior of the considered deep defect level. But since the defect levels for interstitial titanium are quite established [9], a relation of the considered deep defect level to an interstitial state is not very probable. A comparison with literature values suggest a cross-contamination of the sample with vanadium or chromium, both having a defect level being located at $E_C \sim 0.45$ eV. However, the analysis presented here shows the excellent sensitivity of lifetime spectroscopy for recombination-active defects, being able to access reliably the defect parameters of this deep defect center.

Temperature-dependent analysis of the shallow defect level lead to two possible solutions, one being located in the minority- and another in the majority carrier band gap half of silicon. Comparison with literature values measured by means of DLTS strongly suggests that the solution in the band gap half of the minority carriers represents the true energetic defect parameter, $(E_C - E_t)_{\text{sh}} = 0.08^{+0.05}_{-0.02}$ eV.

ACKNOWLEDGEMENTS

The authors thank T. Trupke and R.A. Bardos (now with B.T. Imaging) from the University of New South Wales / Centre of Excellence for advanced Silicon Photovoltaics and Photonics for providing the original photoluminescence measurement setup and fruitful discussions. M.R. would like to thank sincerely the Evangelisches Studienwerk e.V. Villigst and T.R. thanks the Deutsche Bundesstiftung Umwelt (DBU, Germany) for their scholarships.

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