TITANIUM-RELATED DEFECT LEVELS IN SILICON ANALYZED BY TEMPERATURE-DEPENDENT PHOTOLUMINESCENCE LIFETIME SPECTROSCOPY

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ABSTRACT

Temperature-dependent lifetime spectroscopy allows for the determination of defect parameters (like ratio of the carrier capture cross sections and energy level) of point-like defects in silicon. This necessitates reliable measurements of the low-level injection excess carrier lifetime. Photoluminescence-based measurement techniques have been shown to be ideal for this kind of measurements at room temperature, being immune to several measurement artifacts like minority carrier trapping or depletion region modulation. In this contribution it will be shown how the effect of photon reabsorption influences the temperature-dependent photoluminescence measurements and how this can be accounted for using a theoretical model based on the generalized Planck equation. An intentionally titanium-contaminated silicon sample is used to demonstrate this significant effect experimentally. Defect parameters of two independent recombination centers will be presented, which titanium introduces into the silicon band gap.

INTRODUCTION

In the past decades, great efforts have been made to identify and analyze the electrical properties of metal impurities in silicon. Knowledge of the defect parameters, energy levels within the band gap and capture cross sections is of both theoretical and technological interest. Due to the strong influence of material quality on the efficiency of solar cells, analyzing recombination-active defects, introduced for example during crystal growth or solar cell processing, is an important task especially in the field of silicon photovoltaics.

With temperature-dependent lifetime spectroscopy [1], the symmetry factor (ratio of the carrier cross sections $k = \sigma_n/\sigma_p$) and the energy level E_t of point-like defects within silicon can be accessed. For this purpose, the low-level injection (LLI) excess carrier lifetime has to be measured for varied temperatures. From the subsequent fitting of the measurement data with an advanced Shockley-Read-Hall [2, 3] (SRH) model, the defect parameters can be extracted.

Measurements of the true LLI lifetime using photoconductance based methods can be interfered with the known effects of carrier trapping [4] and depletion region modulation [5], resulting in artificially high carrier lifetimes, which do not represent the actual SRH lifetimes which in turn are essential for subsequent modeling. Recently it was shown that photoluminescence based lifetime measurement techniques are not prone to these measurement artifacts [6, 7], making this technique an ideal tool for lifetime spectroscopic analysis.

PHOTOLUMINESCENCE THEORY

In general, the photoluminescence (PL) intensity, I_{PL}, is proportional to the product of the electron and hole densities n and p, respectively:

$$
\begin{aligned}
I_{PL}(t) &= A_i\ B(T,n,p)\, n(t)\, p(t) \\
&= A_i\ B(T,n,p)\big(N_{dop} + \Delta n(t)\big)\Delta n(t) \quad,
\end{aligned}
\tag{1}
$$

where $B(T,n,p)$ is the coefficient of the radiative recombination [8, 9] and A_i is a proportional constant. In order to calculate absolute carrier lifetimes from the measured PL intensity, the above equation is solved for Δn. Together with the independently monitored generation rate G the effective carrier lifetime can be determined [10]:

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

The factor A_i has to be calibrated for each sample by using the self-consistent method [11] or by comparison with photoconductance based measurements like quasi-steady-state photoconductance [12].

PHOTON REABSORPTION

The effect of photon reabsorption within the silicon sample, however, makes this calibration only valid for certain circumstances: If the fraction of the reabsorbed photons (and hence the fraction of the emitted photons) changes, the calibration constant A_i has to change as well. Two mechanisms are conceivable, which may alter the fraction of the reabsorbed photons. Firstly, the absorption probability changes with temperature due to temperature-dependent absorption coefficients, and secondly, the

optical path length of the PL photons within the sample influences the absorption probability. This optical path length depends on the position of the detector and the carrier distribution within the sample, which itself depends on the carrier lifetime and the generation profile. In contrast to measurements at room temperature, where photon reabsorption can be neglected under most circumstances [13], simulations have revealed that it is more severe under elevated temperatures [14] and has to be taken into account for temperature-dependent lifetime spectroscopy (see also Fig. 1).
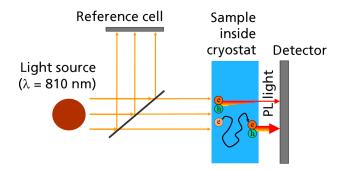

Fig. 1: *Schematic of the quasi-steady-state photoluminescence (QSS-PL) measurement setup. The sample is mounted within a liquid nitrogen cooled cryostat allowing temperatures from 77 K to approximately 590 K to be accessed. The sample is illuminated from the front using an appropriate LED light source. The generation rate is determined independently using an external reference cell while the emitted photoluminescence photons of the sample are detected from the rear using a silicon sensor. Due to the temperature-dependent photon reabsorption the intensity of PL light being emitted depends on the depth within the sample where it originates from (the two extreme cases are shown in the above figure).*

To distinguish the influence of the photon reabsorption from other optical parameters during calibration, it is appropriate to separate the calibration factor A_i into two parts:

$$A_i = B_i \, \xi_i(T, \tau) \quad , \qquad (3)$$

where B_i depends on the optical parameters of the sample and the sensor geometry while ξ_i accounts for the influence of the changing photon reabsorption within the sample (T represents the temperature and τ the carrier lifetime).

Based on the generalized Planck equation [15] for radiative recombination, these reabsorption effects can be taken into account analytically, resulting in a sample-thickness-dependent correction matrix $\xi_i(T, \tau)$ [14]. With this correction matrix, the calibration is valid for different temperatures and carrier lifetimes, even if B_i is calibrated only at one given temperature and carrier lifetime.

EXPERIMENTAL SETUP & SAMPLE PREPARATION

In our experimental setup (see Fig. 1) [16] the sample is illuminated from the front by a LED light source (λ = 810 nm). Radiative recombination of photogenerated carriers within the sample results in the emission of photoluminescence, which is detected by a photodetector located on the rear of the sample. The generation rate is determined from the incident light intensity, which is monitored separately using a calibrated reference cell. For temperature-dependent measurements a liquid nitrogen cooled cryostat was integrated into the PL measurement system, allowing temperatures from 77 K to approximately 590 K to be accessed.

The silicon floatzone (FZ) sample (thickness 600 µm) investigated in this contribution was intentionally contaminated with titanium (Ti) during solidification and has a boron base doping concentration of $N_A = 1.6 \times 10^{15}$ cm^{-3} (ρ = 8.5 Ω cm). To minimize the effect of surface recombination on the effective carrier lifetime, the sample has been passivated by a 70 nm silicon-nitride (SiN$_x$) layer deposited via plasma-enhanced chemical vapor deposition on both sides of the wafer, resulting in a very low surface recombination velocity [17].

MEASUREMENT RESULTS

Calibration of the PL signal was accomplished by comparing the measurement data at 304 K with quasi-steady-state photoconductance measurements. All subsequent corrections due to photon reabsorption were performed in relation to this calibration. Based on the measured optical reflectance of the sample and the sample thickness and doping concentration, simulations have been carried out in order to obtain the reabsorption correction factors ξ_i dependent on different carrier lifetimes and temperatures (see Fig. 2).
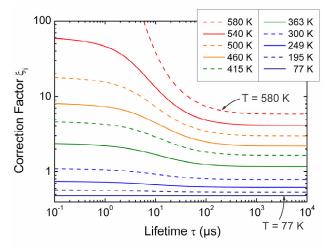

Fig. 2: *Calculated temperature- and carrier lifetime dependent correction factors ξ_i for the 600 µm thick titanium-contaminated silicon sample. For the calculations, the generalized Planck equation was used.*
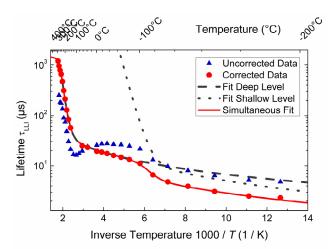
Fig. 3: Measured temperature-dependent low-level injection lifetime (TDLS) of the titanium-contaminated silicon sample. The data have been measured using the improved PL setup with the integrated cryostat. The triangles represent the original measurement data, while the circles represent the data which are corrected for the temperature- and lifetime-dependent photon reabsorption within the silicon. The lines represent the modeled data that have been obtained using a least square fit of a SRH-model featuring two independent defect levels.

The uncorrected temperature-dependent low level injection lifetimes of the titanium-contaminated silicon sample were acquired using a constant calibration factor, without taking photon reabsorption effects into account. These values are shown in Fig. 3 as triangles [16]. Artifacts like a local minimum around $T = 100°C$, which can not be explained by SRH theory, are observed. The ξ-corrected data, which include the effect of photon reabsorption, are shown in Fig. 3 as circles. The strong influence of photon reabsorption on the measured lifetimes is obvious.

In contrast to the uncorrected data, the corrected data can be fitted using a SRH-model featuring two defect centers, which are dominating the lifetime in different temperature regions (dashed and dotted lines in Fig. 3).

The superposition of these two defect centers (solid line in Fig. 3) agrees very well with the corrected measurement data.

Combining these modeling results with injection-dependent lifetime spectroscopic analysis (see Fig. 4), we were able to extract the defect parameters of the two independent recombination-active defect levels being related to titanium in this sample using the defect parameter solution surface (DPSS) method [1]. The results are summarized in Tab. 1. The defect level at $E_C - 0.24$ eV deduced here from lifetime spectroscopy agrees very well with a defect level found in DLTS measurements [18]. In addition, a deep defect level at $E_C - 0.49$ eV was found which was not observed in DLTS measurements, showing the excellent sensitivity of lifetime spectroscopy for recombination-active defects.
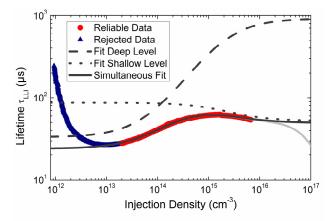

Fig. 4: Measured injection-dependent excess carrier lifetimes of the titanium-contaminated silicon sample. The data have been acquired using a standard QSSPC [12]. Abnormal high lifetimes have been measured below an injection density of 1×10^{13} cm^{-3}, which have been rejected for subsequent modeling. The lines represent the modeled data that have been obtained using a least square fit of a SRH-model featuring two independent defect levels.

Tab. 1: Reported energy levels for titanium in silicon. The data have been evaluated by means of deep-level transient spectroscopy (DLTS) or lifetime spectroscopy (LS). While the DLTS technique is capable of measuring the minority carrier capture cross section, the LS techniques can determine the ratio of the carrier cross sections, known as symmetry factor k.

Energy level E_t (eV)	Capt. cross sect., Symmetry factor	Technique	Reference
$E_C - (0.08 \pm 0.01)$	$\sigma_n = 3.5\times10^{-14}$ cm^2	DLTS	Graff [18]
$E_C - (0.24 \pm 0.03)$	**$k = 7650$**	**IDLS & TDLS**	**this work**
$E_C - (0.27 \pm 0.01)$	$\sigma_n = 1.3\times10^{-14}$ cm^2	DLTS	Graff [18]
$E_C - (0.49 \pm 0.03)$	**$k = 25 \pm 12$**	**IDLS & TDLS**	**this work**
$E_V + (0.289 \pm 0.005)$	$k = 12.0 \pm 0.7$	N_{dop}-IDLS	Rein [1]
$E_V + (0.28 \pm 0.01)$	$\sigma_p = 1.9\times10^{-16}$ cm^2	DLTS	Graff [18]

CONCLUSION

In conclusion, in this contribution the influence of photon reabsorption on temperature-dependent carrier lifetime measurements has been investigated. It was shown experimentally that photon reabsorption has a strong influence on the measured lifetimes, especially at high temperatures. We resolved these limitations by a simulation-based correction, which is easily possible for different temperatures and different carrier lifetimes.

Modeling of the corrected temperature-dependent low-level injection lifetime data of an intentionally titanium-contaminated silicon floatzone sample resulted in an identification of two distinct defect levels. In combination with an injection-dependent analysis it was possible to access the defect parameters of both recombination-active defect levels unambiguously, showing the excellent sensitivity of lifetime spectroscopy for recombination-active defects.

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