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On the benefits of counting single photoluminescence photons for the investigation of low injection lifetime and traps in silicon

Friedemann D. Heinz*, Wilhelm Warta, Martin C. Schubert

Fraunhofer ISE, Heidenhofstr. 2, 79110 Freiburg, Germany

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ABSTRACT

The time correlated single photon counting (TCSPC) technique offers a high sensitivity to low light intensities and a wide dynamic range from nanoseconds to seconds. In this paper we demonstrate the versatility of TCSPC for purposes of the highly sensitive electric characterisation of silicon, complementing the established analogous PL characterisation metrology. Using TCSPC we show that the charge carrier lifetime in silicon may be determined down to very low injection levels of $10^6\ \mathrm{cm}^{-3}$ with a purely dynamic approach. By observing the decay characteristics of the charge carrier density in Cz silicon in the nanosecond to second time regime we obtain the up to now most unambiguous support for the existence of two deep electron trap levels located in the band gap of silicon.

1. Introduction

In the past decade PL spectroscopy on silicon proved to be a versatile approach to characterize silicon for solar cells by detecting the PL emission using semiconductor diodes [1] or CCD arrays [2]. In this paper we outline that the TCSPC technique yields an extraordinary sensitivity to the dynamics of excess charge carriers in silicon, giving rise to a highly sensitive means for the measurement of the charge carrier lifetime. Early applications of TCSPC to silicon investigating Auger recombination kinetics trace back to Beck and Conradt in 1973 [3], Dziewior and Schmidt in 1977 [4] and Hangleiter in 1985 [5]. In 2015 it was shown that this technique may determine the charge carrier lifetime from nanoseconds to milliseconds within a small crystal volume as a function of injection level in a self-consistent way [6] using pulsed and square wave modulated excitation. This approach thus complements the established methods to measure the charge carrier lifetime which evaluate the photoconductance (PC) and photoluminescence (PL) in quasi-steady state (QSS) conditions: QSSPC [7] and modulated PL [8]. While these two methods are easily applicable and deliver robust and reliable charge carrier lifetimes, the TCSPC based technique already overcame two of their restrictions: (1) the limitation to lifetimes above about 1 μs and (2) the minimum sample area of about 1 cm^2.

In this paper we find that the high sensitivity of TCSPC may be exploited to infer the charge carrier lifetime at very low injection conditions. Low injection lifetime spectroscopy is of particular importance for silicon material characterisation, as it delivers a key input to fundamental research on recombination kinetics and defect parameters. In this paper we employ this highly sensitive means for accessing the low injection lifetime to investigate the phenomenon occurring in Cz silicon of apparently high lifetimes at low injection levels with photoconductance or infrared absorption based measurements. Two origins of this phenomenon are controversially discussed in literature: the trapping effect and the effect of depletion region modulation. Our findings substantially contribute to the ongoing discussion on the trapping effect, a detailed introduction of which is given in Section 4.

2. Experimental setup

The experimental setup is depicted in Fig. 1. Parallel excitation of the silicon sample is done with a pulsed laser diode with a wavelength of 640 or 905 nm. The Gaussian laser spot size on the sample has a half width of 831 nm. Approximated square wave excitation is realised by running pulse trains with an 80 MHz pulse repetition rate. The laser intensity is recorded in situ using a silicon single photon avalanche diode. Emitted photoluminescence photons are detected with an ultra-low noise (< 4 cps) InP photomultiplier tube (PMT) operating in Geiger mode. A compound of a silicon filter with anti-reflection coating optimised at 1100 nm and a dielectric edge filter attenuates spurious laser light. The time resolution is obtained using the TCSPC technique. With the used components a temporal resolution of well below 1 ns is obtained.

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* Corresponding author.
E-mail address: friedemann.heinz@ise.fraunhofer.de (F.D. Heinz).

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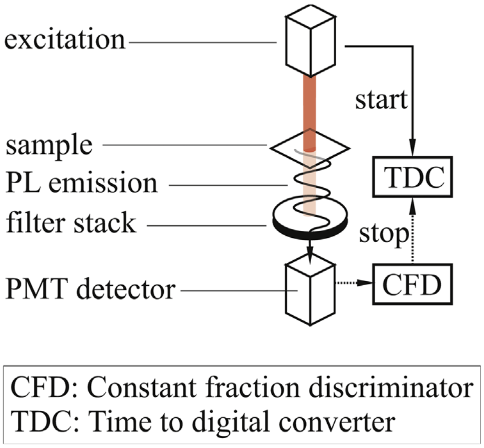

Fig. 1. SPC setup.

The sample is placed directly on the filter stack close to the PMT entrance window to obtain a high solid angle of detection. The surface opposite the detector is illuminated, i.e. the sample is measured in transmission. Reabsorption of PL within the silicon sample is incorporated in all calculations.

3. Low injection charge carrier lifetime

Recording the PL response of a silicon sample upon harmonically modulated excitation is a versatile approach to access the charge carrier lifetime in a self-consistent way [1,9], and in particular in [6] it was shown that when using TCSPC to record the PL response, quasi-square wave modulated excitation (i.e. a train of closely spaced laser pulses) may be used. Two scenarios promise for a higher detection efficiency compared to such modulated excitation: pulsed excitation and non-harmonically modulated excitation. Non-harmonic modulated excitation, which still enables for a self-consistent calibration as described in [6], shall denote the combination of a short lasing period (i.e. short pulse train) with a length $T_{P,1} \sim \tau$ where τ is the charge carrier lifetime which is followed by a period without illumination with a length $T_{P,2}$ which fulfills, e.g.,

$$\exp\left(-\frac{T_{P,2}}{\tau}\right) < 10^{-5} \tag{1}$$

that is, about five orders of magnitude of injection level are covered within the decay time. This is demonstrated by means of a p-type FZ sample (thickness $W=25\,\mu\text{m}$ and doping density $n_A = 1.9\times10^{16}\,\text{cm}^{-3}$). Fig. 2(a) shows the measurements of the PL decay using $T_{P,1} = 1.75\,\text{ms}$ and $T_{P,2} = 8.25\,\text{ms}$ leading to an injection level ranging over 5 orders of magnitude shown in Fig. 2(b). From Fig. 2(b) it can be seen that low injection levels of below $10^7\,\text{cm}^{-3}$ may be accessed. In Section 4.3.2 we show a measurement reaching injection levels of $10^6\,\text{cm}^{-3}$. If the calibration factor of the setup is known single excitation pulses may be used for excitation. Single pulses offer the advantage, that the initial conditions are well-known: the measured photon flux per pulse J_{pH} directly delivers the initial condition of the time dependent equation of continuity. Single pulses are used in Section 4.

4. Evaluation of the trapping effect in Czochralski silicon

The trapping of minority charge carriers became generally known as causing a measurement artefact with PC based techniques. Charge carriers are trapped by centres with an energy level located in the band gap and released relatively slowly compared to the charge carrier recombination lifetime. When evaluating the conductivity decay curve down to low excess charge carrier densities, this leads to an apparently high lifetime as the trapped carriers cause an increase of the majority carrier density [10–12] via the mechanism of dielectric relaxation: in order to sustain charge carrier neutrality, the majority carrier density increases if traps are filled while keeping the minority carrier density constant. The same effect is observed when evaluating the free-carrier emission of silicon, possibly with spatial resolution [13,14]. For PC decay measurements, the slow release of minority charge carriers causes a long tail in the decay curve [15–18].

Fan [19], and Hornbeck and Haynes [18,20] proposed a kinetic model to describe the population of the trap levels postulating a mechanism based on multiple trapping of excess charge carriers. They observed two trap levels in silicon crystals and could give, with considerable experimental effort, estimates for all trapping parameters. Macdonald and Cuevas found that it is possible to extract the trap centre density N_t and the ratio of the trapping and release time constants τ_t/τ_g from single QSSPC measurements [12] assuming one trap level.

Although often occurring in the context of a measurement artefact, trapping may be a source of information on the electronic structure of defects in silicon. Yet, the origin of traps is not clear. However, different trends and correlations were found. Recent studies found a correlation to dislocations [11,13,14], to oxygen [17,21], and to thermal donors [17].

Up to now, all methods applied for the investigation of traps were based on a measurement of the occupation number of traps n_t. This is rooted in the fact, that photoconductance and free carrier emission are sensitive to the sum of electrons and holes. Under steady state or quasi-steady state condition the minority charge carrier density is pinned by the generation rate. The trapped electrons thus lead to an increase of the majority charge carrier density by n_t (by dielectric relaxation). The photoluminescence intensity I_{pl} is sensitive to the product of electron and hole densities, such that (for p-type silicon under low level injection conditions)

$$\begin{aligned} I_{pl} &\propto np - n_i^2 \\ &\approx (n_A + n_t)\Delta n_e \end{aligned} \tag{2}$$

as the minority hole concentration $n_h = n_A + n_t + \Delta n_h$. The minor influence of the trap density in Eq. (2) (for all samples in this paper $n_A \gg n_t$) leads to the insensitivity of the PL intensity with respect to traps.

While this consideration applies to steady state or quasi-steady state measurements of the PL intensity, traps may alter the recombination kinetics significantly for a measurement of the transient decay of the PL intensity. In Fig. 3(a) and (b) the photoluminescence decay after short light pulses recorded using TCSPC is shown, revealing different decay constants which anti-correlate to the PL intensity, a salient feature of trapping.

This section commences with discussion on the possible effect of a depletion region modulation on a transient decay of the charge carrier density. In Section 4.2 the experimental procedure and the observed effects in the decay curves and the calculated lifetimes are described. In the following section, the obtained lifetime curves are interpreted and modelled assuming a multiple trapping mechanism. By modelling the charge carrier dynamics, it becomes possible to determine all trap parameters, i.e. the trap capture time, the escape time, the trap density as well as their capture cross section and energy level in p-type silicon. Finally, the determined parameters are discussed in the context of the findings in the literature in Section 4.3.3.