

**EFFECTIVE EXCESS CARRIER LIFETIMES EXCEEDING 100 MILLISECONDS IN
FLOAT ZONE SILICON DETERMINED FROM PHOTOLUMINESCENCE**
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ABSTRACT: Effective excess carrier lifetimes of 130 ms are reported for 1000Ωcm float zone silicon wafers. These values, which are four times larger than the highest effective lifetimes reported for silicon before, are obtained experimentally from transient and from quasi-steady state photoluminescence measurements. It is shown that photoluminescence measurements are a very useful and sensitive technique for determining the effective lifetime even at low injection levels. We also show that the lifetimes measured with quasi steady state photoluminescence are not significantly affected by excess charge that is accumulated in space charge regions, an effect that can lead to a dramatic overestimation of the lifetime, when determined by other techniques such as photoconductance.

Keywords: Photoluminescence, Lifetime, Silicon

1 BACKGROUND

Recent investigations of high resistivity silicon samples revealed that well-passivated silicon can be a quite efficient light emitter. Internal (IQE>20%) and external (EQE=6.1%) photoluminescence quantum efficiencies were reported for float-zone wafers at room-temperature [1].

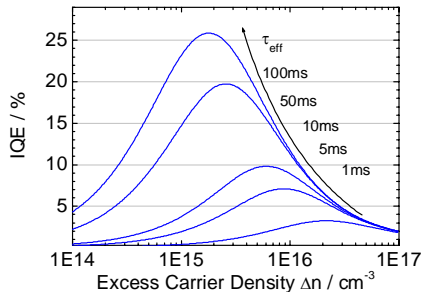


Figure 1: Internal luminescence quantum efficiency in a 1000Ωcm n-type wafer as a function of injection level for different low-injection effective lifetimes.

The IQE can be modelled as the ratio of the radiative recombination rate within a sample over the total recombination rate. The results of such model calculations, in which analytical expressions for Coulomb-enhanced Auger-recombination and for Coulomb-enhanced radiative recombination, respectively were taken into account, are shown in Fig.1. All other recombination mechanisms, such as surface recombination, junction recombination and bulk-Shockley-Read-Hall-recombination were lumped in that simplified model into a constant effective excess carrier lifetime τ_{eff} . The latter generally depends itself on the excess carrier concentration Δn . For our purposes the assumption of a constant τ_{eff} is, however, a good approach to highlight the minimum effective lifetime that is required to achieve a given IQE. Fig.1 shows that effective lifetimes >50ms are the theoretical *lower limit* for an IQE > 20%. Given that the IQE of 20% was

reported in [1] as a lower bound, lifetimes on the order of 50-100ms are expected in these wafers, values that are about two to three times higher than the highest effective lifetimes (32ms) reported for silicon so far [2]. The aim of the present study is to confirm the theoretically predicted extremely high τ_{eff} experimentally using photoluminescence and photoconductance experiments.

2 LIFETIME TECHNIQUES

2.1 Photoconductance (PC)

PC-measurements are widely used in photovoltaics to characterize silicon samples [3, 4]. With this technique the variation of the effective lifetime with injection level (Δn) can be monitored quickly, conveniently and in a contact-less mode over a wide injection level range. Depending on the order of magnitude of the lifetimes to be measured transient- and quasi steady state (QSS) PC-measurements and also measurements in an intermediate mode [5], in which the decay of the PC-signal is on the same order of magnitude as the generation-rate, are routinely employed.

A problem in PC measurements, that can lead to an erroneous assignment of the lifetime occurs in the presence of space charge regions [6, 7]. In space charge regions electrons and holes are spatially separated and the recombination activity is therefore not representative of the bulk material properties. As a result the lifetime determined from PC is not representative of the bulk and surface recombination processes in the sample if the excess carriers in the space charge region contribute significantly to the total excess carrier density.

Charge trapping is another mechanism that can lead to an erroneous determination of the lifetimes in transient and QSS-PC measurements [8].

2.1 Photoluminescence (PL)

An alternative lifetime technique that has not been employed extensively in the past is PL. An important point that sets PL apart from most other methods is that the measured signal is proportional to the *product* of minority and majority carrier concentrations while in

other lifetime techniques their *sum* is measured.

The total rate of spontaneous emission R_{sp} inside a sample is given as $R_{sp} = B(T) \cdot n_e \cdot n_h$, with n_e and n_h the electron and hole concentrations, respectively and $B(T)$ the radiative recombination coefficient, which is assumed to be constant for injection levels $< 10^{15} \text{cm}^{-3}$. R_{sp} can also be expressed as a function of the intrinsic carrier concentration n_i :

$$R_{sp} = B(T) \cdot n_i^2 \cdot \exp\left(\frac{\Delta\eta}{kT}\right) \quad (1)$$

The PL is thus directly related to the separation of the Quasi-Fermi levels $\Delta\eta$. On the other hand the voltage of a solar cell is ideally given as $V = e\Delta\eta$. A PL-measurement performed on a silicon wafer thus actually represents a *contact-less voltage measurement*.

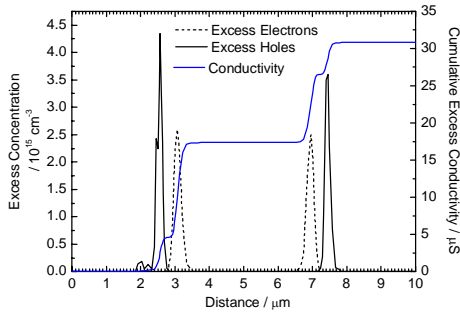


Figure 2: Excess carriers in space charge regions in an n-type sample with junctions on both sides dominate the total excess conductivity at low light intensities.

An advantage of QSS-PL over QSS-PC is that PL-measurements are by far not as strongly affected by the presence of space charge regions, as demonstrated by the PC1D simulation shown in Fig.2. Here, a $10\mu\text{m}$ thick $1\Omega\text{cm}$ n-type sample with Gaussian profile p-type doping (10^{19}cm^{-3}) on both sides was simulated. The illumination was monochromatic (870nm) with an intensity of $1\mu\text{W}/\text{cm}^2$. Fig.2 shows the excess electron and hole concentrations and the cumulative excess conductivity. The total excess conductivity is completely dominated by the spatially separated carriers in the space charge regions. Note, that this result would also apply to a much thicker wafer of a few hundred microns. The thickness of only $10\mu\text{m}$ was chosen here purely for presentation purposes.

The same PC1D simulation shows that the separation of the quasi-Fermi energies is almost constant (425 meV) with only marginal variations of less than 0.2meV throughout the sample. In a wafer with a typical thickness of a few hundred microns the space charge regions with reduced recombination rate only consist a small fraction of the total wafer volume. Thus, even if the major fraction of excess carriers is accumulated in space charge regions, the steady state PL signal is still dominated by the much larger field-free bulk regions of the wafer.

QSS-PL-measurements thus appear to be the method of choice for lifetime measurements as they are more robust against experimental artifacts due to space charge regions and thus more representative of the bulk properties of the samples, which we are interested in here.

In contrast to QSS-PL measurements, the influence of space charge regions can be fairly strong in *transient* PL measurements. If the majority of excess carriers is stored in the space charge region, then the temporal decay of the excess carrier concentration in the bulk, and thus of the PL signal can be strongly affected by the dynamics at which charge carriers recombine in- and diffuse out of the space charge region.

3 THEORY

For the determination of the lifetime the excess carrier concentration Δn must be extracted from the measured PL data. For an n-type wafer the measured luminescence intensity I_{lum} can be written

$$I_{lum} = A_i \cdot R_{sp} = A_i \cdot B(T) \cdot (N_D + \Delta n) \cdot \Delta n \quad (2)$$

A scaling factor A_i has been introduced in Eq.2 between the rate of spontaneous emission (which is a microscopic, not directly measurable quantity) and I_{lum} . We thus assume that the relation between the rate of spontaneous emission and I_{lum} is linear, which is a reasonable assumption for high-lifetime wafers firstly because the separation of the quasi-Fermi levels is constant throughout the thickness and secondly because the optical material properties of the sample do not change under illumination conditions typically encountered in PV. From Eq.2 Δn is given as

$$\Delta n = -\frac{N_D}{2} + \sqrt{\left(\frac{N_D}{2}\right)^2 + \frac{I_{lum}}{A_i \cdot B(T)}} \quad (3)$$

Using the derivative of Eq.2 and with $d\Delta n / dt = G(t) - \Delta n / \tau_{eff}$ we find

$$\tau_{eff} = \frac{\Delta n}{G(t) - \frac{dI_{lum}}{dt} \cdot \frac{1}{(N_D + 2 \cdot \Delta n) \cdot B(T) \cdot A_i}} \quad (4)$$

With Eq.4 and Eq.3 the effective lifetime can be calculated from PL measurements in the transient, intermediate and QSS mode. Our Eq.4 is equivalent to the generalized analysis that has been introduced by Nagel et al. for PC-measurements [5]. It simplifies to

$$\tau_{eff} = \frac{I_{lum}}{B(T) \cdot A_i \cdot N_D \cdot G(t) - \frac{dI_{lum}}{dt}} \quad (5)$$

for low-injection conditions. Under low injection conditions, where the luminescence signal is linear in Δn , the analysis of PL measurements is thus equivalent to the analysis of PC measurements, with the only additional complication that the scaling factor A_i must be determined.

4 EXPERIMENTS

We investigated commercially available 4-inch $570\mu\text{m}$ thick textured $1000\Omega\text{cm}$ Unisil n-type wafers, which were passivated with a 600nm thermal oxide. An additional and in most cases quite significant reduction of the surface recombination was achieved by charging the

oxides on both sides of the wafer using an electrostatic gun. A modified SINTON flash-tester was used for PC measurements. A $2 \times 2 \text{ cm}^2$ silicon pin-diode in combination with a low noise preamplifier was used as PL sensor. The choice of silicon as a sensor for the PL of silicon samples is obviously not ideal because only the short wavelength tail (about 10% of the total PL signal) of the emitted photon flux can typically be detected. A sensor with a slightly lower band-gap would be more suitable but was not available for this study. With a germanium sensor the entire PL signal from a silicon sample can be measured, however the increased photo-generation is overcompensated by significantly larger thermal noise. A silicon detector was thus the best compromise available. The PL sensor was incorporated into the flash-tester so that PL and PC measurements could be performed simultaneously. To be able to measure ultra-long lifetimes in the intermediate or QSS mode the flash-lamp was replaced by a 870nm high-power LED-array package with a rated maximum optical cw-output power of 1.5 W. The LED-array illuminated the investigated wafers homogeneously.

The PL sensor was located directly behind the investigated wafer and did not receive any excitation light as the peak emission of the LED at 870nm is entirely absorbed by the wafer. An additional 900nm short pass filter was placed between the LED and the wafer in order to block the very weak long wavelength tail around $\lambda > 1150\text{nm}$ in the emission of the LED to avoid the detection of that emission by the PL-sensor.

Computer control of the LED output and parallel data readout of up to three channels from a 16-bit data acquisition card allowed measurements over a very wide dynamical range of more than four orders of magnitude with a single measurement and also convenient averaging of arbitrarily large numbers of individual acquisitions of the same waveform. As a result very small excess carrier concentrations of $< 10^{11} \text{ cm}^{-3}$ could be accurately determined with this system.

The generation rate $G(t)$ and the scaling factor A_i must be determined experimentally for PL-lifetime measurements in the intermediate and QSS mode.

A_i can be determined from Eq.3 if the measured PL-signal and the corresponding excess carrier concentration Δn (the latter in absolute units) are known at least at one given injection level. As shown below the absolute data for Δn from PC are most reliable at large excess carrier concentrations. We measured PL and PC for identical illumination conditions, which allowed A_i to be determined from Eq.3. Once the scaling factor A_i for a particular wafer is determined it can be used for the entire injection range and for both transient and QSS measurements. The recombination coefficient $B(T)$ need not be known throughout the analysis as it can be lumped into the scaling factor.

The generation rate $G(t)$ in our set-up is linear in the total incident light intensity because the spectrum of the LED and the absorptance of the samples both do not change with light intensity. The temporal dependence of the incident light intensity was measured simultaneously with the PL signal with a silicon sensor and a low-gain preamplifier. A glass plate was used to couple a fraction of the incident light from the excitation source into the sensor.

For the lifetime analysis the measured relative values

of $G(t)$ must be converted into absolute values, which can be accomplished using a recently developed self-consistent method [9]. This method is based on the fact that the analysis of the $\tau_{\text{eff}}(\Delta n)$ -data in the rising and in the falling branch of a temporal excitation profile only agree in the intermediate mode if the measured values of $G(t)$ are scaled correctly. Because this method only works reliably in an injection range where trapping has a small effect on transient measurements, the calibration of the relative $G(t)$ data was performed at large injection levels.

5 RESULTS

Fig.3 shows the temporal dependence of Δn as determined from a transient PC-decay measurement (top curve). Also shown in Fig.3 is the excess carrier concentration from PL-decay measurements under identical illumination conditions. Good agreement between the curves is observed in the initial stage of the decay.

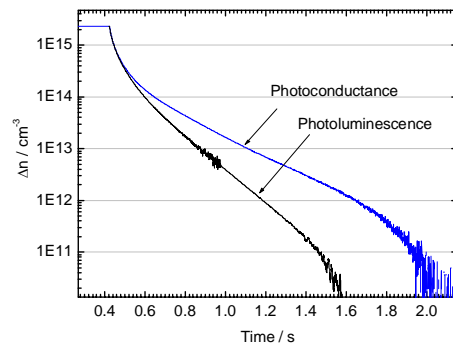


Figure 3: Transient PC and transient PL measurements on a 1000 Ωcm n-type silicon wafer measured under identical illumination conditions.

Fig.3 shows strong deviations between the results from the transient PC-decay and from the PL-decay. The PC decays extremely slowly with a maximum decay time of 240 ms. The origin of this extremely slow decay and of the deviations between PL and PC is not conclusively clarified yet, but it is most likely due to either the space charge accumulation effect or due to charge trapping.

Because charge trapping can have a significant influence on the decay-time in transient PL measurements we also carried out QSS-PL measurements in order to confirm that the observed decay time obtained from PL is representative of the lifetime and not of a trapping-related time-constant.

A modified sine wave was used in the QSS measurements as the temporal excitation profile. Due to the extremely long effective lifetimes the variation of the excitation must be on the order of tens of seconds to reach near QSS-conditions. Fig.4 shows the PL signal (scaled by A_i) and the relative variation of the generation rate (self consistently determined from the measured incident light intensity).

The effective lifetime determined from the data in Fig.4 is plotted in Fig.5 together with the results from the transient PL measurement from Fig.3. A lifetime of $\tau_{\text{eff}}=130 \text{ ms}$ is found around injection levels of $\Delta n = 10^{13} \text{ cm}^{-3}$ and good agreement is observed between

the transient- and QSS-PL data for carrier concentrations $>10^{13}\text{cm}^{-3}$. At lower injection levels we observe deviations in the lifetimes determined from the transient and from the QSS-PL data. The origin of

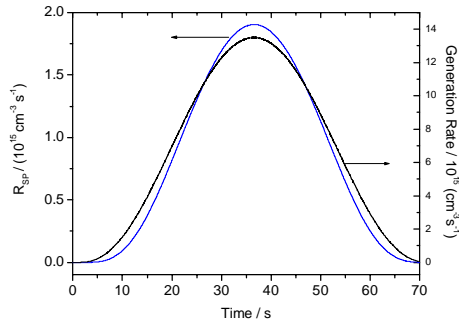


Figure 4: QSS-PL measurements. The curves represent the measured luminescence intensity and incident light intensity, which were scaled as described in the text to give the rate of spontaneous emission and the generation rate, respectively.

these deviations is not clear at this stage. Trapping or the influence of space charge regions on the transient PL data are possible explanations. The good agreement of the lifetimes determined from transient PL and from QSS PL at larger injection levels, however indicates that these lifetimes are not strongly affected by these effects. A further strong indication that these high lifetimes are representative of the bulk properties is that the value of $\sim 40\text{ms}$ at injection levels around 10^{15}cm^{-3} is in good agreement with the predictions of the simplified theoretical model for the luminescence quantum efficiency from Fig.1.

6 CONCLUSIONS

We have shown that effective excess carrier lifetimes of 130 ms can be determined from transient and QSS photoluminescence measurements. Because PL measurement, in particular in the QSS mode, are fundamentally less sensitive to the accumulation of charge carriers in space charge regions they represent a more robust experimental technique to characterize samples to be used in photovoltaics than PC. It should be mentioned that the space charge region effect also strongly affects *all* other lifetime techniques in which the *sum* of minority and majority carriers is measured.

The slightly more complicated analysis of PL data requires knowledge of the doping concentration and an independent measurement of the absolute value of Δn at least at one injection level in order to be able to scale the values from PL and to determine the excess carrier concentration. The separate determination of A_i could in principle be avoided if the luminescence intensity was measured in absolute units. In practice, however such absolute measurements are generally connected with relatively large experimental errors, which would result in corresponding errors in the determined lifetime. A combination of PL and PC thus appears to be the most reliable and practical compromise.

The lifetime could be determined in this study over an injection level range of four orders of magnitude, which, due to the square law dependence of the

luminescence intensity on Δn at high injection conditions corresponds to a variation of the PL signal over almost seven orders of magnitude. Due to the averaging capabilities of our system very low excess carrier concentrations could be determined ($\sim 10^{11}\text{cm}^{-3}$) accurately. These concentrations correspond to a separation of the quasi-Fermi levels of roughly 300meV in a 1000 Ωcm wafer. In wafers with a higher doping level (e.g. 10^{16}cm^{-3}) the same separation of the quasi-Fermi energies corresponds to even lower excess carrier concentrations of only $\sim 10^8\text{cm}^{-3}$ detectable in PL, showing that in this case PL can actually be much more sensitive than PC.

We only used one commercially available LED package so far, and that one about a factor two below its maximum rated output power. By reducing the illuminated area and with ten LED packages operated in parallel and at maximum power we expect to be able in the near future to reach light intensities equivalent to about 100 Suns, which are sufficient for most applications in photovoltaics.

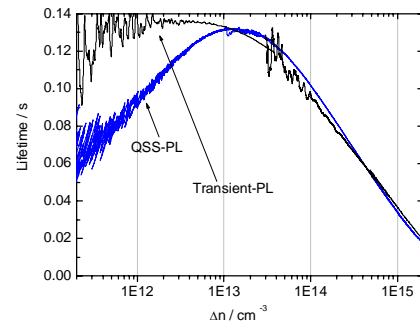


Figure 5: Effective excess carrier lifetime extracted from the transient PL measurements from Fig.3 and from the QSS-PL measurements from Fig.4.

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