On using photoconductivity decay to determine Si free carrier recombination lifetime: possibilities and challenges

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Abstract. Free carrier recombination lifetime (τ) in Si single crystals is a parameter, that characterizes the quality of the material. The primary procedure for τ measurement in ingots is photoconductivity decay (PCD) analyses, including contactless μ-PCD and eddy current methods. One of the main problem in this methods is a surface recombination influence on the PCD curve. It is usually assumed that in ingots the influence of surface recombi

nation can be neglected. Well-known dependence of effective lifetime (τ eff) on τ, surface recombination velocity (S) and sample thickness (d) describes the maximum value of a lifetime. Based on the numerical calculations of the one dimensional continuity equation we have shown that if the sample thickness exceed 5L D, the maximum lifetime cannot be achieved before PCD signal decline to 5% of maximum, so the question arises what is the interval of the decay curve where the experimental value of the τ eff has to be determined. We used the range from 45-5% of the maximum PCD signal following the recommended SEMI MF 1575 standard (τ SEMI). The dependencies of τ SEMI on τ, d and S were calculated for different versions of PCD measurements and measurement equipment. The recommended thickness for lifetime measurements of non-passivated samples is in the range (1-5)L D. The hardware capabilities of contactless methods are compared.

1. Introduction

In semiconductors, unlike in metals, the charge carriers concentration can be widely changed at constant temperature due to doping level and generation/recombination processes. In direct-bandgap materials, basic recombination mechanism is radiative recombination-dependent on the concentration of free charge carriers. In indirect-bandgap semiconductors basic mechanism is a Shockley-Read-Hall (SRH) process: the electron passes from conductivity band to valence band through energy states created within the bandgap by an impurity. The free carrier recombination lifetime (τ) is inverse proportional to deep level impurities concentration (DL) [1, 2]. Therefore τ in the non-direct-bandgap material, like Si and Ge, is a main quality characteristic as well as the resistivity. From measurements of recombination lifetime in indirect-bandgap semiconductors the concentration of DL can be detected with high precision (<10¹⁰ cm⁻³) that is impossible with other methods.

The most common method to measure the recombination lifetime in a semiconductor without making any structures or contacts to sample is photoconductivity decay measurements. The are some contactless PCD measurement techniques that allow estimating the parameter on ingots and single-crystal wafers before the production process begins [2-10].
There is a fundamental problem of PCD curve analysis. Relaxation curve is strongly affected by the surface recombination velocity \( S \) [6-10]. In 1955, the work was published where analytical expressions for charge density distribution and time dependence in light illuminated samples were obtained [11]. It was proposed to take into account the influence of the surface recombination as the boundary conditions for solving the continuity equation and take into account the first term in the expansion of the carrier flux concerning the excess carrier concentration on the surface \( \Delta n(0,d) \). In this case, \( S \) was the parameter determining the relation between the flux and \( \Delta n(0,d) \). In [11] was shown that the relaxation curve is described as the sum of exponents. Contributions of each one depend on the initial charge density distribution \( \Delta n(0,\lambda) \). Characterization times depends on the diffusion coefficient \( D \), sample thickness \( d \), and \( S \):

\[
\tau_{\text{eff}}^{-1} = \tau^{-1} + \tau_S^{-1} = \tau^{-1} + 4\xi D/d^2
\]  

(1)

Parameter \( \xi \) can be obtained from transcendental equation [11, 12]:

\[
\cot \xi = 2\xi D/dS
\]  

(2)

The maximum value of \( \xi \) in (2) from the first quadrant define the maximum value \( \tau_{\text{eff}} = \tau_{\text{max}} \). Exact solution for \( \tau_{\text{max}} \) can be obtained in two extreme cases: for \( dS \to \infty \), \( \xi = \pi/2 \) (infinity surface recombination velocity case):

\[
\tau_{\text{eff}}^{-1} = \tau^{-1} + \frac{\pi^2 D}{d^2}
\]  

(3)

and for \( d \to 0 \) (thin sample case):

\[
\tau_{\text{eff}}^{-1} = \tau^{-1} + \frac{2S}{d}
\]  

(4)

In [13], by numerical solution it was shown that, in general, \( \tau_{\text{max}} \) can be defined with great accuracy as a sum of those two cases:

\[
\tau_{\text{eff}}^{-1} = \tau^{-1} + \left( \frac{d}{2S} + \frac{d^2}{\pi^2 D} \right)^{-1}
\]  

(5)

Obviously, in ingots with non-passivated surfaces and large \( d \), it can be expected that the measured effective lifetime will be equal to the bulk lifetime. Unfortunately, in quite many investigations concerning the influence of various factors on the determination of recombination lifetime, it is not discussed in which part of the relaxation curve the above maximum value of the effective lifetime is reached [2-10].

Based on a numerical solution of the continuity equation in papers [12-14] it was shown that when sample thickness rise, the relative contribution of the "fast" exponents increases. To calculate the \( \tau_{\text{eff}} \), it was proposed to use the recommendations of the SEMI MF1535 standard [15] and calculate \( \tau_{\text{eff}} \) as the slope of the logarithm of the relaxation curve in the interval from 45-5% of the maximum signal intensity (\( \tau_{\text{SEM}} \)).

The work aims to analyze the influence of the main factors which affect the shape of the PCD curve for non-passivated samples and to determine the conditions of the applicability of Eqs. (3-5) to the calculation of the bulk carrier lifetime (\( \tau \)) using its effective experimental value.

2. **Thickness influence on the PCD curve**

The one-dimensional continuity equation was solved by a finite difference method. The simulation was carried out for samples of n- and p-type silicon single-crystals. The samples thickness varies from 0.5 to 16 mm, \( \tau \) varies from 10 \( \mu \)s to 10 ms, \( S \) varies from 10 to \( 10^4 \) cm/s, and the illuminating LED wavelength (\( \lambda \)) ranges from 0.8 to 1.107 \( \mu \)m. The limitation of the penetration depth of the microwave field in semiconductor takes into account by integration of excess concentration in the bounded area.

In [12] it was shown, that for a frequently used wavelength 1.06 \( \mu \)m for \( \tau \) varying from 10 to \( 10^4 \) \( \mu \)s (this interval includes most popular \( \tau \) values for microelectronics) correlation between \( \tau_{\text{SEM}} \) and \( d \) have
a generalized form if the thickness is expressed in units of diffusion length ($L_D^2 = D\tau$). If the sample thickness is less than $5L_D$, expression (5) can be used. Moreover, if the thickness is in the range of $(1-5)L_D$, a more simple Eq. (3) can be used. In this case, it is not necessary to know the value of surface recombination velocity. Consider the value of differential lifetime, defined as the cotangent of the inclination angle of the dependence of the logarithm of the excess concentration $\Delta n$ on time $t$ ($\tau_d = -\left(\frac{\partial \ln \Delta n}{\partial t}\right)^{-1}$). Dependencies of $\tau_d$ on dimensionless time $t/\tau_{max}$ for n-type silicon samples with different thickness are shown in figure 1. Curves were calculated using the following parameters: $\tau = 700 \mu$s ($L_D = 1 \text{ mm}$), $S = 10^4 \text{ cm/s}$ (unpassivated surface).

**Figure 1.** Dependence of the differential lifetime for samples with different thickness. The arrows indicate the time at which the excess concentration is 45% and 5% of the maximum.

**Figure 2.** The variation of the differential lifetime for the sample with $d = L_D$.

**Figure 3.** The variation of the differential lifetime for the sample with $d = 5L_D$.

**Figure 4.** The variation of the differential lifetime for the sample with $d = 1.5L_D$.

It can be seen in figure 1 that for a small thickness saturation of the differential lifetime is established almost instantly. With a further increase of the thickness, the contribution of "fast" surface exponents increases, and for $d > 5L_D$, $\tau_{SEMI}$ will be noticeably lower than expected by (5). Two reasons may cause this decline. The first one is a magnification of fast surface exponents contribution to the decay curve. The second one relates to inhomogeneity of the generation of the excess charge carriers across the thickness. Increasing of the effective lifetime for several quadrants of Eq. (2) is shown in figure 2-4. The circles indicate the time on the relaxation curve, at which the exponents from different quadrants
decrease by a factor of e (2.718).

As can be seen in figures 2-4, an increase in the sample thickness leads to an expansion of the characteristic times of the surface exponents. When the thickness of the sample is less than 5L_D, relaxation curve becomes monoexponential starting at the level of 45% of the maximum.

3. Influence of light wavelenght on the PCD curve

The wavelength of illuminating LED influence on the homogeneity of generation of excess charge carriers because of different value of absorption coefficient \( \alpha \). In figure 5, it is shown how \( t_{SEMI} \) depends on the inverse absorption coefficient. Also in the figure marked the typically LED wavelength used in modern measuring devices.

![Figure 5. The relation between the effective lifetime and the inverse absorption coefficient \( \alpha^{-1} \) of single-crystal silicon. Colored vertical lines indicate thicknesses of those samples. Simulations were carried out for n-type silicon with \( \tau = 700 \mu s \) (\( L_D = 1 \text{ mm} \)).](image)

As can be seen in figure 5, for thicknesses of \((1-3)L_D\), the effective lifetime does not depend on the illumination wavelength, and it can be calculated from (3). For \( d > 5L_D \) and LEDs with \( \lambda < 1 \mu \text{m} \) \( t_{SEMI} \) changes from (3) and goes to saturation when average photon mean free path until absorption is equal to the thickness of the sample.

From the viewpoint of the uniformity of the minority carrier distribution, the best light emitting diodes for the excitation is the 1.1 \( \mu \text{m} \) ones. However, the small absorption coefficient of silicon (\( \alpha = 0.375 \text{ cm}^{-1} \)) leads to a PC signal being too low for the registration. Thus, the LED with \( \lambda = 1.05 \mu \text{m} \) (\( \alpha = 18.3 \text{ cm}^{-1} \)) may be considered optimal because in this case the deviation from the values calculated using Eq. (3) does not exceed 5%, regardless of thickness. The best for the measurements is a sample thickness of \((1-5)L_D\). For such samples one can choose LEDs with high absorption coefficients (\( \lambda = 0.9 \mu \text{m}, \alpha = 314 \text{ cm}^{-1} \)).

4. Skin-layer limiting effect

For contactless methods of the photoconductivity decay detection, two methods can be used: absorption of a microwave signal by free charge carriers (\( \mu \)-PCD method) and the change in the quality factor of the RC circuit (transient eddy current HF methods) [9, 10, 14-18].

The influence of the illumination wavelength is equally relevant for both \( \mu \)-PCD and HF methods. But the \( \mu \)-PCD has limitations that make the HF method more suitable. First of all, skin effect limits the depth of penetration of the electromagnetic field into the conducting material. The skin effect will be manifested if the thickness of the sample exceeds the thickness of the skin layer. In this case, a decrease in frequency, for example from 10 GHz, recommended in SEMI 1535 [16], to 2.5 GHz (all other things being equal) increases the depth of the skin layer by a factor of 2 (see table 1). The effect on the measurement results will be observed when the thickness of the skin layer is less than 5L_D. For resistivity
above 1 Ω·cm, the maximum lifetime is limited by recombination through impurity centers. For the concentration of impurity centers of $10^9 - 10^{10}$ cm$^{-3}$, the maximum lifetime is 10 - 1 ms ($5L_D > 5 - 26$ mm), respectively. As can be seen from table 1, the use of the recommended frequency for measuring non-passivated samples with long lifetimes can lead $\tau_{SEMI}$ to values estimated by (3), even if the thickness of the sample lies in the optimal range from the viewpoint of use (4). From this point of view, the HF method is also advantageous, since for MHz frequencies the thickness of the skin layer is from one to hundreds of centimeters.

**Table 1.** Dependence of the thickness of the skin layer (mm) on the frequency of the electromagnetic field and resistivity.

| $f$, GHz | 0.01 | 0.1 | 1  | 10 | 100 |
|----------|------|-----|----|----|-----|
| 3.2 E-2  | 8.9  | 28.1| 88.9| 281.2| 889.2|
| 2.5      | 1.0  | 3.2 | 10.1| 31.8| 100.6|
| 5.0      | 0.7  | 2.2 | 7.1 | 22.5| 71.1 |
| 10       | 0.5  | 1.6 | 5.0 | 15.9| 50.3 |
| 34       | 0.3  | 0.9 | 2.7 | 8.6 | 27.3 |

We make an analysis of PCD curve for a low level of injection of the excess free carrier. With a high level of injection, the differential lifetime in the material depends on the level of injection: it will decrease with the decrease of the signal. Taking into account this factor requires exact knowledge of the initial carrier concentration and maximum nonequilibrium concentration, e.g., leads to a significant complication of measurement devices.

5. **Experimental investigation**

To verify the simulation results FZ-grown n-type single-crystal silicon wafers were measured. The resistivity of silicon was 2500 Ω·cm. Samples were cut out from the same ingot, so the bulk lifetime was the same for samples of different thickness. A thickness of the samples varied from 1 to 32 mm. The measurements of the PCD curve were carried out by µ-PCD method [16]. Samples were illuminated with IR-LED ($\lambda = 1.06$ µm). Results of measurements ($\tau_{SEMI}$) are shown in table 2.

**Table 2.** Measurement results for single-crystal silicon wafers.

| Thickness, mm | 32  | 5   | 2   | 1.2 |
|---------------|-----|-----|-----|-----|
| Thickness/$L_D$, a.u. | 21.3| 3.3 | 1.3 | 0.8 |
| $\tau_{SEMI}$, µs | 1350 ± 130 | 820 ± 80 | 230 ± 20 | 91 ± 8 |
| $\tau$, µs    | 1380 ± 150 | 1600 ± 200 | 1540 ± 600 | 1400 ± 800 |

The evaluation of $\tau$ based on $1/\tau_{eff}$ dependence on $1/d^2$ (3) gives $D = 15 ± 1.5$ and $\tau = 1550 ± 150$ ($L_D \approx 1.5$ mm).

Substituting these values of $D$ and $d$ into Eq. (3) $\tau$ can be estimated (see $\tau(3)$ in table 1). It can be seen, that for samples with the thicknesses of 2 mm and 5 mm $\tau(3)$ is close to the expected $\tau$. For 1.2 mm sample $\tau(3)$ is less because the equation (5) must be used, but we don't know $S$ exactly.

In [13], it was shown that for single-crystal silicon samples with thicknesses above $5L_D$, the following equation could be used for $\tau$ calculation:

$$\tau = A \exp \left( -\frac{d}{\delta} \right) + t_0$$  (6)

where $d$ is the sample thickness [cm], and $\tau$ is the recombination lifetime [s].

The following dependences of parameters $A$, $\delta$ and $t_0$ on $\tau_{eff}$ [s] were obtained:

- $A = 600 \tau_{eff}^{1.3}$, $\delta = 1.9 \tau_{eff}^{0.4}$, $t_0 = 1.6 \tau_{eff}^{1.083}$ for n-type single-crystal silicon;
A = 31000 \tau_{\text{eff}}^{1.4}, \delta = 2.2 \tau_{\text{eff}}^{0.41}, t_0 = 1.6 \tau_{\text{eff}}^{-0.033} \text{ for p-type single-crystal silicon.}

For the 32 mm sample, it can be obtained \tau = 1680 \pm 200.

In figure 6, the logarithm of normalized PCD curves is plotted versus dimensionless time \( t/\tau_{\text{max}} \). PCD signal was normalized to the level of 5\% of maximum value. The circles indicate the time at which the excess conductivity reached 45\% of the maximum value.

Figure 6. The normalized PCD signal and differential lifetime in silicon wafers.

From figure 6 it can be seen that the distortion of the initial part of the relaxation curve strongly depends on the sample thickness. The part of the relaxation curve for \( \tau_{\text{SEMI}} \) calculation is almost linear if sample thickness is less than \( 3L_D \).

6. Conclusions

✓ Numerical simulation of the decay curve and differential lifetime shows that, for non-passivated samples, attaining the lifetime value described by the well-known Eq. (5) depends on the relative sample thickness. When calculating the effective lifetime using the interval between 45\% and 5\% of the maximum signal intensity, as recommended by SEMI MF 1535 (\( \tau_{\text{SEMI}} \)), (5) may be used for the calculation of the bulk lifetime for thicknesses up to \( 5L_D \).

✓ At thicknesses above \( 5L_D \), the maximum lifetime value is not achieved because of the increasing contribution of faster components to the decay curve, so that a numerical simulation must be used for a correct calculation of the bulk lifetime.

✓ In the interval from \( L_D \) to \( 5L_D \), it is possible to use the convenient formula considering an infinite recombination rate (3).

✓ For thicknesses up to \( 5L_D \), the \( \tau_{\text{SEMI}} \) value practically does not depend on the wavelength of the excitation light. For thicker samples, \( \tau_{\text{SEMI}} \) depends on the excitation wavelength and achieves a maximum value when the sample thickness does not exceed the inverse light absorption coefficient.

✓ The lifetime calculation error will be smaller if the PCD curve is detected by the eddy current technique.

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