Presented at the 25th European PV Solar Energy Conference and Exhibition, 6-10 September 2010, Valencia, Spain

DETERMINING THE MINORITY CARRIER LIFETIME IN EPITAXIAL SILICON LAYERS BY MICRO-WAVE-DETECTED PHOTOCONDUCTIVITY MEASUREMENTS

D. Walter[1], P. Rosenits[1], F. Kopp[1,2], S. Reber[1], B. Berger[3] and W. Warta[1]
[1]Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstraße 2, 79110 Freiburg, Germany
[2]now at Osram Opto Semiconductors Leibnizstraße 4, 93055 Regensburg, Germany
[3]Institute of Theoretical Physics, TU Bergakademie Freiberg, Leipziger Straße 23, 09596 Freiberg, Germany
Tel: +49 761/4588-5661; Fax: +49 761/4588-9250; Email: Dominic.Walter@ise.fraunhofer.de

ABSTRACT: Measurements of effective lifetimes on epitaxial silicon thin-film material have been carried out. Two different methods were used for this purpose: one is the well established Microwave-Detected Photoconductivity Decay (µPCD) method as commercially available from Semilab, and second the more recent Microwave-Detected Photoconductivity (MDP) method introduced by Freiberg Instruments. Both methods are critically analyzed and compared in regard to their applicability in the sector of epitaxial silicon layers. The investigation includes a modeling of the expected measurement signal for both measurement conditions. The results, obtained from a large number of lifetime samples investigated in this study and consisting of different qualities of the silicon substrate as well as different qualities of the epitaxial layer, support the conclusion that both of the above mentioned methods may be used to determine the effective lifetime of a silicon thin-film sample.
Keywords: Minority carrier lifetime, microwave-detected photoconductivity decay, crystalline silicon thin-films

1 INTRODUCTION

Crystalline silicon thin-film solar cells are being developed as a promising alternative to bulk silicon solar cells. To obtain high efficiencies in crystalline silicon thin-film solar cells, it is very important to understand the physical influence of among others the substrate material on the electrical quality of the epitaxial layer. Therefore, reliable methods to extract key properties of the epitaxial layer, such as the effective lifetime, are needed. Conventional measurement schemes are hampered by the low signal due to the small layer thickness and the relatively small expected lifetime. The applicability of commercially available microwave-detected photoconductivity measurements on silicon thin-film samples is tested using two different measurement techniques: the µPCD [1, 2] method and the MDP method [3].

2 EXPERIMENTAL SETUP

2.1 Microwave Detected Photoconductivity Decay (µPCD)

The extraction of the effective lifetime of the minority charge carriers within a semiconductor sample by means of the µPCD measurement method is based on the change of the reflectance of a microwave when irradiated on the sample. A short laser pulse, with a constant pulse width of $t_p = 200$ ns optically generates excess charge carriers. This change of the excess charge carrier density is directly linked with a change of the conductivity of the sample. The microwave reflectance of the sample is a function of the reflected power divided by the irradiated power, which can be developed in a Taylor series. If only first order terms are taken into account the changes in the conductivity are linearly correlated with the reflected power. Low-level injection conditions safely ensure this correlation. Therefore it is possible to monitor the time dependence of the integrated charge carrier density by observing the power of the reflected microwave. Over a certain time range, corresponding to the effective lifetime of the sample, changes of the integrated charge carrier density, referred to as excess carrier transient, are recorded. After the laser is switched off, the conductivity decreases monoexponentially (after a possible faster initial decay) and can be fitted with an exponential curve to extract the effective lifetime at a given position of the sample.

A widely known problem of the µPCD method is that in order to obtain a good signal-to-noise ratio, usually a high excitation rate is needed, i.e. a high photon flux at the surface of the sample of $g \approx 6{\cdot}10^{21}$ (cm²·s)$^{-1}$, which can be varied within an order of magnitude. This implies that low-level injection conditions, used in the theoretical derivation, are not fulfilled in general. However, this problem can be overcome by taking only those parts of the transient into account where the excess charge carrier density has already decreased sufficiently and is small compared to the doping concentration of the semiconductor sample. Also a bias light can be used in order to obtain a smaller deflection from the steady-state charge carrier density. When considering only lifetimes in the low-level injection regime, injection dependence of the lifetime will not have a major impact on the effective lifetimes extracted. Of course, this is only the case if trapping and any injection dependent surface recombination can be neglected.

The measurement setup used in this contribution is the commercially available WT-2000 tool distributed by Semilab Semiconductor Physics Laboratory Co. Ltd. A block diagram of the basic principle of a microwave-detected photoconductivity measurement is shown in Figure 1.

Using this tool makes it possible to create effective lifetime maps over the whole sample. Different spatial resolutions are possible, but it should be mentioned that the used optics in this setup leads to a constant, approximately 1 mm² wide excitation area which is superimposed to the maximum lateral resolution of the xy-table of only 125 µm.

2.2 Microwave Detected Photoconductivity (MDP)

In MDP, as compared to the µPCD measurement setup, an additional microwave cavity is used, which enhances the sensitivity. Theoretically the setup is treated as if the semiconductor sample is placed inside the cavity and therefore becomes a part of the dielectric medium. A laser beam with variable pulse lengths up to t_p =1 ms generates excess charge carriers within the sample, which leads to a variation of the polarization of the sample under investigation. This variation is linked to changes of the dielectric constant, which itself is connected to the conductivity of the sample. The slightest changes of the electrical properties of a dielectric medium within a cavity lead to measurable changes of the resonant frequency and the attenuation of the cavity-sample system. These changes can be detected similarly to the µPCD setup; however whereas the change in the reflectance of the sample is monitored in the latter, MDP measures the change in the reflectance of the cavity, which is caused by variations of the dielectric properties of the sample under investigation. In this contribution, an excitation rate of $g \approx 1{\cdot}10^{20}$ (cm²·s)$^{-1}$ is used.

In practice, the sample is not placed inside the cavity but is coupled to the dielectric medium through an opening in the bottom of the cavity, which is positioned a short distance (smaller than 1 mm) above the sample. Similarly to the µPCD setup, the detection head is movable and therefore maps can be created. The resolution of the lifetime map may be chosen up to 0.3 mm, when a laser spot diameter of 0.28 mm and a resolution of the xy-table of 0.2 mm are used. The measurement setup used in this contribution is the commercially available MDPmap, distributed by Freiberg Instruments.

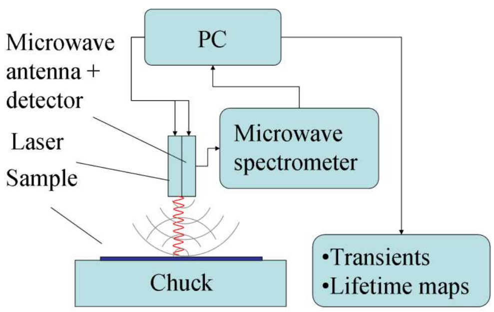

Figure 1: Basic principle of a microwave-detected measurement. The MDP measurement setup uses an additional cavity to detect the light induced changes of the conductivity of the sample.

2.3 Comparison of the Measurement Conditions

The most significant difference in the measurement conditions is due to the different excitation pulse width. At MDP measurements, usually much longer excitation times are chosen than at µPCD measurements. This difference leads to different distributions of the excess charge carrier density within the sample. At MDP conditions, a steady state excess charge carrier profile during the excitation period can be obtained in contrast to µPCD conditions. This fact enables the MDP setup to not only measure the effective lifetime, but also the absolute change in the conductivity of the sample independently when the photoconductivity saturates during the excitation. For thick silicon wafers the distribution of the excess charge carrier density was simulated by N. Schüler et al. [4], resulting in the conclusion that with MDP conditions the maximum of the excess charge carrier distribution is located deeper inside the sample than with µPCD conditions.

3 THEORY

3.1 The Model

To predict the transients of the MDP and µPCD measurements, in the present approach a model presented by H. Väinölä et al. [5] was chosen and applied to the geometries and properties of the samples in this contribution.

The model is based on solving the continuity equations for the excess charge carrier density in the crystalline silicon epitaxial layer and the crystalline silicon substrate. The following simplifying assumptions are made for the analytical solution: (1) Measurements are performed under low-level injection conditions, (2) independence of the bulk lifetime and surface recombination velocity of the excess charge carrier density, (3) lateral homogeneity of bulk lifetime within the epitaxial layer and the substrate. Furthermore, (4) the diffusion length of the minority carriers is assumed to be small compared to all lateral dimensions of the measurement setup and the sample geometry, allowing a one dimensional treatment of the problem, and (5) the common assumption that every photon which is absorbed in the sample generates an equal number of electrons and holes.

It has to be mentioned that the model does not include an additional recombination path at the interface between the epitaxial layer and the substrate other than the diffusion of the charge carriers into the substrate and vice versa.

For this study the model of H. Väinölä et al. was slightly extended in order to take the impact of band gap narrowing in highly doped silicon into account, by referring to Schenk [6].

In spite of the simplifications, simulated transients obtained by this model are in good agreement with Buczkowski et al. [7] for the case of a one-layer system. Thus we can use this approach for an approximate comparison of major differences resulting from the different measurement conditions for our epitaxial layer system. It has to be noted, that e.g. the high injection effects in the initial part of a µPCD-transient are not represented correctly.

3.2 Simulation Results

First of all, the qualitative characteristics of the transients at different measurement conditions were analyzed. The geometrical and electrical properties of the sample, i.e. the thickness of the epitaxial layer and the substrate w_{epi} and w_{sub}, respectively, the Shockley-Read-Hall lifetime in the epitaxial layer and the substrate τ_{epi} and τ_{sub}, and the doping concentration N_{epi} and N_{sub} in the epitaxial layer and the substrate, respectively, were chosen as representing a typical sample under investigation. A well passivated front surface with recombination velocity s_{front} = 10 cm/s, s_{back} = 10^4 cm/s were used.

The different measurement conditions are characterized by the pulse width t_p, the incident photon flux at the surface of the sample g and the wavelength of the excitation laser λ. In our simplified model the value of the incident photon flux only shifts the simulated transient along the Δn- or $\Delta\sigma$-axis and does not have an impact on the shape of the curve. The pulse width and laser wavelength, in contrast, play a major role. For the thicknesses, w_{epi} = 40 µm and w_{sub} = 500 µm were chosen for the epitaxial layer and substrate respectively. All further parameters of the simulation are given in Table I.

Table I: Simulation parameters used for the qualitative analysis of the decay transients.

τ_{epi} / µs	τ_{sub} / µs	N_{epi} / cm^{-3}	N_{sub} / cm^{-3}
10	1	$1\cdot10^{16}$	$1\cdot10^{18}$
		t_p / µs	λ / nm
MDP		100	978
µPCD		0.2	978

Figure 2 shows the result of the simulation, the two expected decay transients. As mentioned earlier the steady state condition, i.e. a constant, time-independent charge carrier profile within the sample, is reached at MDP measurement. By comparing the two transients, it is obvious that both transients exhibit the same asymptotic decay constant, i.e. the same effective lifetime (in this case $\tau_{eff} = 9.14$ µs), but there is a difference at the beginning of the decay, immediately after the excitation is switched off. In Figure 2 the rectangular excitation pulse is switched off at $t = 100$ µs, starting at $t = 0$ µs for the MDP measurement and at $t = 100$ µs – 0.2 µs for the µPCD measurement.

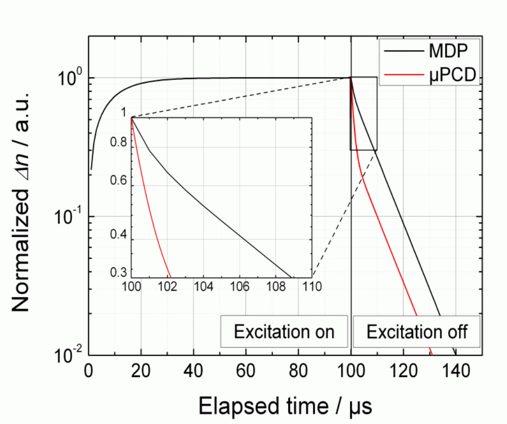

Figure 2: Simulation of the transient of the excess charge carrier density under MDP and µPCD conditions using the parameter described in the text.

As discussed in literature for wafers [7], the initial part of the transient, after the excitation is switched off, depends mainly on the surface recombination strength and the penetration depth of the generation light, whereas the latter part is influenced by both surface and bulk recombination effects.

In order to understand the different behavior of the transients under the two different measurement conditions, we investigate the influence of the duration of the excitation for different wavelengths. Pulse width is $t_p = 100$ µs for MDP and $t_p = 0.2$ µs for µPCD conditions. The varying parameter is the absorption coefficient α, which was varied between 10 and 10000 cm^{-1}, corresponding to wavelengths of the excitation between 510 and 1060 nm [8]. To point out the differences between different thicknesses of the epitaxial layer, samples with (a) $w_{epi} = 10$ µm and (b) $w_{epi} = 40$ µm with a substrate thickness of $w_{sub} = 500$ µm were simulated. The results of the simulation are shown in Figure 3.

Comparing different excitation wavelengths, i.e. different absorption coefficients in Figure 3, corresponding to different penetration depth between $L_{abs}(\alpha = 10 \text{ cm}^{-1}) \approx 920$ µm and $L_{abs}(\alpha = 10^4 \text{ cm}^{-1}) \approx 1$ µm, using the same measurement method (dashed line for MDP and solid line for µPCD in Figure 3), support the assertion that with longer wavelengths the fast decay at the beginning is more prominent than with shorter wavelengths for both thicknesses of the epitaxial layer and for both measurement conditions. Comparing the different measurement methods using the same excitation wavelength, i.e. the same absorption coefficient, it is obvious that µPCD conditions exhibit a stronger decay than MDP conditions. Again this applies to both thicknesses.

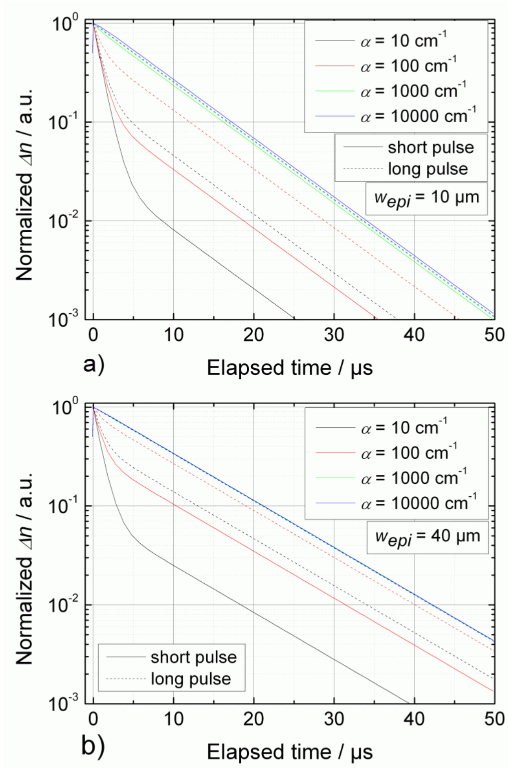

Figure 3: Simulated decay transients under both measurement conditions (MDP: long pulse, µPCD: short pulse) on samples with a) 10 µm and b) 40 µm epitaxial layer thickness.

A possible interpretation of this behavior is as follows: as mentioned earlier, the recombination velocities at the surfaces of our well passivated samples contribute in a minor way to the transients. From previous results we infer that the interface between substrate and epitaxial layer and the low lifetime in the substrate dominate the transient's behavior. Longer wavelengths penetrate much deeper into the sample; therefore, more excess charge carriers are generated in the interface region and the substrate. There the charge carriers recombine with a shorter time constant (in our model $\tau_{sub} = 1$ µs) than in the epitaxial layer and therefore contribute to the short strong decay at the beginning of the transient. Another indication which supports this interpretation is that the first part of the decay is less pronounced in Figure 3 b than Figure 3 a, as a thicker epitaxial layer is simulated and therefore less charge carriers are generated close to and within the substrate (assuming identical wavelengths).

This interpretation explains the differences between excitation wavelengths, the deviation between the two measurement methods (i.e. pulse length) is simply understood by the fact that a short excitation pulse leads to a stronger influence of the higher modes in the initial part of the decay compared to a long excitation pulse [9].

The simulation and theoretical considerations assert that for crystalline silicon thin-film (cSiTF) lifetime samples, measurements based on microwave reflection or absorption are preferably to be carried out using a short excitation wavelength, assuming a well passivated front surface. In this case the fast decay at the beginning of the transient after the excitation is switched off is minimal for both measurement conditions and the asymptotic decay is reached faster. In the measured transients, however, the behavior predicted by the simulations is not found. Two measured transients of the same sample measured with both setups are shown in Figure 4. The decay transients recorded by MDP tend to start delayed and not right after the excitation is switched off. This observation contradicts the behavior expected for the decay of an excess carrier density. µPCD transients usually show a slightly stronger decay right after the excitation but not to the extent expected from Figure 3. These differences are not clarified further here, since, as outlined below, they are of no importance for our purpose. For the difference between both decay transients it may also play a role that in the case of a long excitation built-in traps are usually saturated whereas in the case of a short excitation the beginning of the transient is enhanced by captioning processes. For an improved characterization of the beginning of the transients a simulation approach by rate equations may be necessary [10].

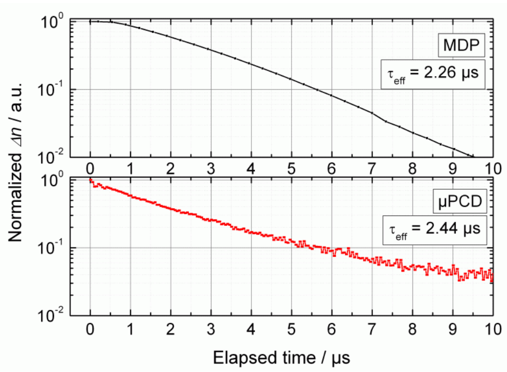

Figure 4: Comparison of two measured transients showing the same effective lifetime. A MDP measurement is shown above, a µPCD measurement below. Comparison of the first part of the transients makes the differing behavior obvious.

Important for our aim - the validation of both measurement methods for determining the recombination behavior - is that the initial effects discussed are expected to be minor for the conditions of our samples from the modeling calculations and that they are indeed found to be minor (albeit different) in the measured curves. The effective lifetimes expected to be equal in any case for these different setups in the asymptotic limit are reached comparably fast, suggesting that both techniques are equally suited to extract effective lifetimes.

4 MEASUREMENT RESULTS

4.1 Sample Preparation

In this study four different groups of samples with a typical sample structure as shown in Figure 5 have been investigated. These groups can be distinguished by the different substrate qualities used. The basic structure of all samples is the same, namely a highly doped p-type crystalline silicon substrate upon which a moderately doped p-type crystalline epitaxial layer is deposited by means of chemical vapor deposition (CVD) at elevated temperatures between 1000 and 1200 °C. The surfaces of the samples under investigation are passivated using Al_2O_3 or SiN_x leading to similar recombination velocities of below 25 cm/s. In all groups the attempt was made to make the thickness of the epitaxial layer the only varying parameter.

The samples of **group A** consist of monocrystalline Czochalski (Cz) substrates and an epitaxial layer deposited at the Institute of Microelectronics in Stuttgart (IMS).

Group B comprises monocrystalline Cz substrates with an epitaxial layer deposited at Fraunhofer ISE.

Group C gathers multicrystalline (mc) silicon substrates and epitaxial layers deposited at Fraunhofer ISE.

The last **group D** consists of substrates fabricated of upgraded metallurgical-grade (umg) silicon and again epitaxial layers deposited at Fraunhofer ISE.

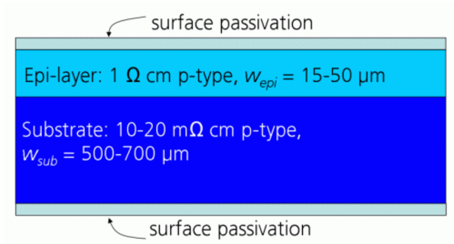

Figure 5: Typical configuration of a lifetime sample under investigation in this work.

4.2 Measurements

To extract one effective lifetime value for a certain crystalline silicon thin-film (cSiTF) sample, effective lifetime maps over the whole sample area are recorded. Two lifetime maps of the same sample carried out with µPCD at 904 nm excitation wavelength and with MDP at 940 nm are shown in Figure 6. For the MDP lifetime map a excitation pulse width of 5 µs was chosen compared to the commonly used 0.2 µs for the µPCD lifetime map.

The maps show different resolutions, the MDP map has a resolution of 0.28 mm compared to the µPCD map with a resolution of 0.5 mm. The sample's dimension is 5x6.5 cm², but the epitaxial layer is only deposited on the 5x5 cm² area in the center. The differences in the absolute value of the lifetimes may be due to a different injection level within the time interval used for the extraction of the decay constant. There may also be an influence by degradation effects of the sample as a time of 6 months lies between the two measurements.

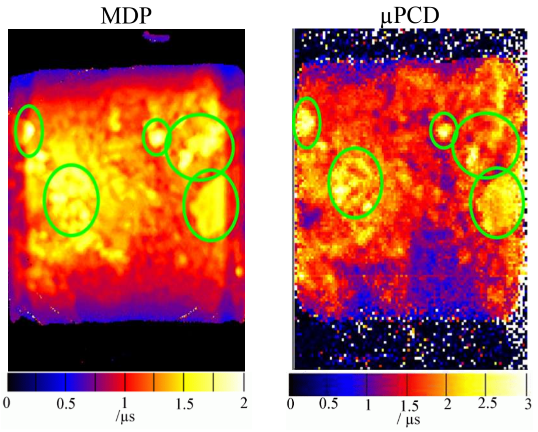

Figure 6: Comparison of two maps of the effective lifetime recorded from the same cSiTF-lifetime sample belonging to group C with an average epitaxial layer thickness of w_{epi} = 45 µm. The map on the left shows a MDP record, whereas on the right a µPCD map is shown. The corresponding excess charge carrier density is in the range of $\Delta n \sim 10^{17}$ cm^{-1} for MDP compared to $\Delta n \sim 10^{18}$ cm^{-1} for µPCD.

As shown by the green circles in Figure 6, there are several structures of the sample's surface which can be clearly seen on both lifetime maps. There is a reasonable agreement between both measurements judged from the structural agreement.

To extract one effective lifetime value for each sample, the arithmetic average of all effective lifetimes extracted from every individual measurement point of the map of one sample is defined as the effective lifetime τ_{eff} of the corresponding sample.

As indicated earlier, different wavelengths for exciting the sample may be used. MDP measurements with excitation wavelengths λ = 660 nm and λ = 978 nm, as well as µPCD measurements with the laser wavelengths of λ = 350 nm, λ = 532 nm and λ = 904 nm were performed.

The extracted effective lifetimes of the measurements performed for group A samples are shown in Figure 7. The colored triangles refer to µPCD measurements and the colored squares refer to MDP measurements. The effective lifetime values of group A vary between 5.5 and 17.8 µs.

Figure 7 shows that with increasing thickness of the epitaxial layer the effective lifetime τ_{eff} increases as well. This applies for all investigated samples. To explain this behavior, either τ_{epi} itself must be dependent on the epitaxial layer thickness or the increase may be due to the impact of the surfaces of the epitaxial layer, i.e. the front surface and the interface between substrate and epitaxial layer.

An increase of τ_{epi} seems unlikely, as from the technological point of view, an increase of the epitaxial thickness is rather supposed to lead to a decrease of the epitaxial quality, as e.g. the sample is exposed much longer to the elevated temperatures during deposition.

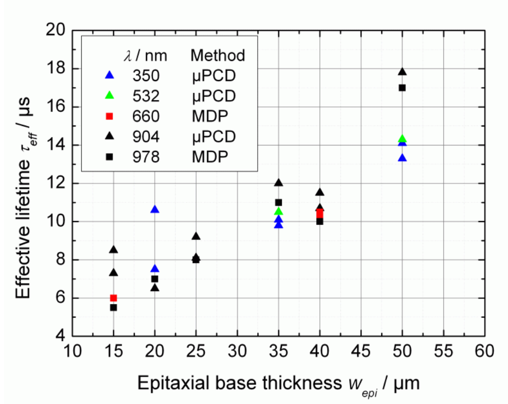

Figure 7: Measured effective lifetimes of group A, monocrystalline Cz-substrate with epitaxial layer deposited at IMS.

The front surfaces of the samples are all well passivated judged from FZ-references processed in parallel. Therefore; we attribute the increase of the effective lifetime mainly to the effects of the interface between substrate and epitaxial layer. Even without any additional recombination via defects at the interface, a net flux of excess charge carrier into the substrate exists, leading to a recombination velocity which is supposed to be an order of magnitude higher than the recombination velocity at the front surface [11].

Secondly, with a closer look on Figure 7 it may be seen that there is no systematic deviation between different wavelengths of the exciting laser found in these measurements. Considering firstly the three different laser wavelengths used for µPCD measurements, i.e. the blue, red and black triangles in Figure 7, it can be seen for epitaxial thicknesses of 20, 35 and 50 µm that the measured effective lifetime spreads, but not with regard to the laser wavelength. Taking additionally into account the measurements performed at group B, shown in Figure 8, this observation is confirmed and extended to MDP measurements. The effective lifetimes of group B vary between 1.1 and 5.9 µs.

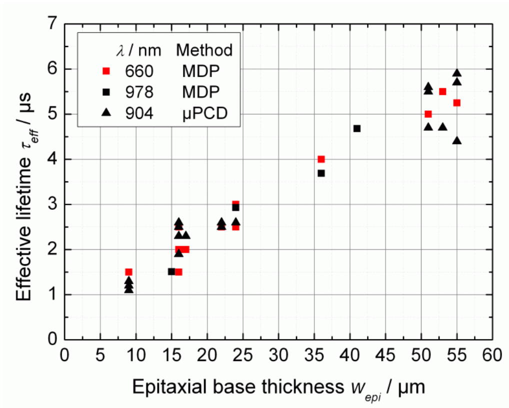

Figure 8: Measured effective lifetimes of group B, Cz-substrate with epitaxial layer deposited at ISE.

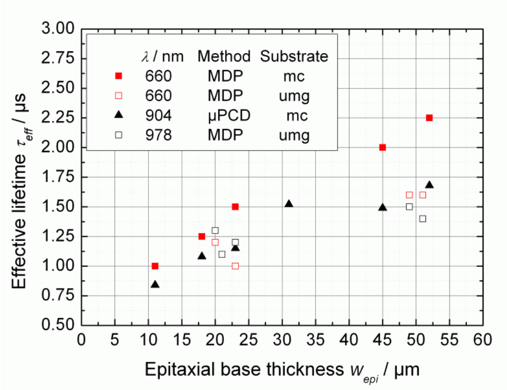

Figure 9: Measured effective lifetimes of group C and group D, mc-substrate and umg-substrate, respectively, with epitaxial layer deposited at ISE.

In Figure 9 the results for group C and group D investigated in this contribution are shown. The effective lifetimes of these samples vary between 0.8 and 2.3 µs. Group C is the only group where the effective lifetime values extracted from MDP and µPCD measurements seem to differ systematically. However this fact can be well explained by systematic differences in the measured lifetime maps occurring for this series of measurements. The µPCD maps show to a certain extent an area on every sample where no lifetime is measurable. In the particular case of group C we can confirm the µPCD map, as with a spreading resistance profiling (SRP) measurement of the area in question the lack of the epitaxial layer becomes obvious. In the respective MDP maps of this series spurious edge effects were visible, which could not be reproduced in a later measurement and were most likely an artifact.

In summary, the measured effective lifetimes do not show any systematic deviations between the two techniques for the samples investigated in this work.

5 CONCLUSION

Microwave-based measurements on a large number of crystalline silicon thin-film lifetime samples have been performed using two different measurement setups. The two setups investigate the sample under two different conditions, which can mainly be distinguished by the duration of the excitation of excess charge carriers. These two different measurement conditions are expected to lead to differences in the first part of the decay of the transients. The asymptotic part of the transients is expected to be no longer affected by the measurement conditions, i.e. the transients show an equal monoexponential decay, which should be reached fast according to our calculations. Consequently, no deviation between the results from the two measurement setups in regard to the extracted effective lifetime of cSiTF lifetime samples can be observed. The effective lifetime are found to be in agreement with expectations from simulations of a corresponding two layer system.

6 ACKNOWLEDGEMENTS

This work has been supported by internal project funding of the Fraunhofer-Gesellschaft in the frame of the "Si-Beacon" project, the European Social Funds (ESF) 2007-2013 with the project number 080940489 and the state of Saxony.

7 REFERENCES

[1] D. E. Kane and R. M. Swanson, in Proceedings of the 18th IEEE Photovoltaic Specialists Conference, Las Vegas, Nevada, USA, 1985, p. 578.

[2] M. Kunst and G. Beck, Journal of Applied Physics 60 (1986) 3558.

[3] K. Dornich, T. Hahn, and J. R. Niklas, in Proceedings of the Materials Research Society Symposium Vol. 864, 2005, p. 148932.

[4] N. Schüler, T. Hahn, K. Dornich, J. R. Niklas, and B. Gründig-Wendrock, Solar Energy Materials and Solar Cells in press (2010)

[5] H. Väinölä, J. Storgårds, M. Yli-Koski, and J. Sinkkonen, Solid State Phenomena 82-84 (2002) 771.

[6] A. Schenk, Journal of Applied Physics 84 (1998) 3684.

[7] A. Buczkowski, Z. J. Radzimski, G. A. Rozgonyi, and F. Shimura, Journal of Applied Physics 72 (1992) 2873.

[8] M. A. Green and M. J. Keevers, Progress in Photovoltaics: Research and Applications 3 (1995) 189.

[9] K. L. Luke and L.-J. Cheng, Journal of Applied Physics 61 (1987) 2282.

[10] S. Schmerler, T. Hahn, S. Hahn, J. R. Niklas, and B. Gründig-Wendrock, Journal of Material Science: Mat. in Elect 19 (2008) 328.

[11] P. Rosenits, F. Kopp, D. Walter, S. Reber, and W. Warta, in Proceedings of the 25th European Photovoltaic Solar Energy Conference, Valencia, Spain, 2010.