LIFETIME STUDIES ON CRYSTALLINE SILICON THIN-FILMS BY PHOTOLUMINESCENCE MEASUREMENTS

P. Rosenits, T. Roth, S. Reber, W. Warta, S.W. Glunz

Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, D-79110 Freiburg, Germany
Phone: +49 761 4588 5269, Fax: +49 761 4588 9250, Email: philipp.rosenits@ise.fraunhofer.de

ABSTRACT: A novel measurement and analysis method of determining individual excess carrier lifetimes in multi-layer systems is presented. This is particularly interesting for the characterisation of crystalline silicon thin-film samples consisting of an electrically active epitaxial layer on top of a crystalline substrate. The analysis principle is based on a comparison between a measured photoluminescence intensity ratio and associated simulated radiative recombination ratios. It benefits from the fact that for low excess carrier lifetimes within the epitaxial layer the carrier concentration in the said layer is limited by bulk recombination, while for high carrier lifetimes surface recombination is dominating. Depending on which excess carrier lifetime is realised, the excess carrier level in the epitaxial layer is either strongly dependent or nearly independent from the epitaxial layer thickness. In order to verify this measurement and analysis principle, results of a set of crystalline thin-film samples with varying epitaxial layer thickness on a highly doped Czochralski substrate are presented.
Keywords: Lifetime, Thin-film, Photoluminescence

1 INTRODUCTION

Crystalline silicon thin-film solar cells are a very attractive and promising alternative to bulk silicon solar cells as they only need a small fraction of costly high-purity silicon while still achieving good efficiencies above 15% [1].

A key parameter for the performance of the finished solar cell is the excess carrier lifetime which characterises the material quality and can directly be translated into an average diffusion length of an electron-hole pair. If, for example, the excess carrier lifetime is low, the open-circuit voltage and therefore the efficiency of the cell is automatically limited correspondingly. Consequently, an easy and reliable method to determine this excess carrier lifetime is of enormous interest for both practical process control as well as the evaluation of the potential and limitations of a specific cell concept.

Unlike standard silicon wafer characterisation, using a whole range of different lifetime measurement methods, such as quasi-steady-state photoconductance (QSSPC) [2], microwave photoconductance decay (MWPCD) [3, 4] or quasi-steady-state photoluminescence (QSSPL) [5], similar characterisation methods for crystalline silicon thin-films are still lacking.

In the following, first steps towards a comprehensive and reliable excess carrier lifetime characterisation of epitaxial thin-film material are presented. The measurement principle as well as the evaluation method is described. The theoretical concept is tested and confirmed by a set of epitaxial crystalline thin-film samples.

2 MEASUREMENT AND ANALYSIS PRINCIPLE

Out of the three major lifetime measurement methods mentioned above – MWPCD, QSSPC and QSSPL – we chose to utilise the latter one as it shows several advantages in case of the specific sample structure of crystalline thin-film material.

The quasi-steady-state photoluminescence lifetime measurement principle is based on the reemission of photons due to direct radiative recombination of excess charge carriers constantly generated by a monochromatic light source. In our QSSPL setup (see Fig. 1) the excitation source consists of a light emitting diode (LED) array of a power up to 0.025 W/cm^2 which is adjustable, so that an excess carrier concentration in a range of 4 to 5 orders of magnitude can be set. As the excitation wavelength is λ=810 nm, which is equivalent to an absorption length of L_{abs}=13 µm in silicon, most of the excess electron-hole pairs are generated in the epitaxial layer if the layer thickness is greater than L_{abs}, which is true in our case.

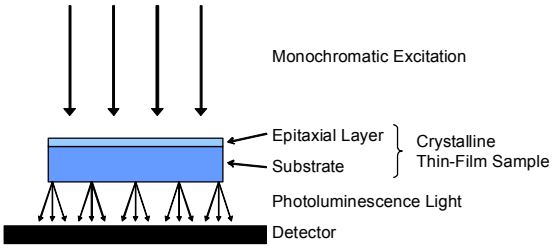

Figure 1: Photoluminescence measurement setup used in this study. The crystalline silicon thin-film sample to be investigated is exposed to monochromatic light with a wavelength of λ=810 nm. Subsequently, the photo-luminescence light emitted at the back side of the sample is detected and evaluated.

For a characteristic time span after their generation the excess carriers recombine via one out of different recombination mechanisms, which is expressed by the so-called charge carrier lifetime. With photoluminescence measurements one can determine the rate of radiative recombination, where the energy released during the recombination process is transformed into the emission of a photon. These photons are emitted in arbitrary directions; however, in the setup used in the work presented here, we only measure the photon emission at the backside of the sample. Note that, contrary to other applications, the detected photoluminescence (PL) signal is neither resolved laterally nor spectrally, as this is not necessary for the

intended approach to determine the excess carrier lifetime.

In general (and neglecting the trapping of excess carriers), the detected photoluminescence signal $I_{PL}(t)$ can be described by the equation

$$\begin{aligned} I_{PL}(t) &= A_i U_{rad}(t) \\ &= A_i \int Bn(x,t)p(x,t)dx \\ &= A_i \int B\left[N_{Dop}(x)+\Delta n(x,t)\right]\Delta n(x,t)dx \end{aligned} \qquad (1)$$

where U_{rad} denotes the rate of radiative recombination, n, p, Δn and N_{Dop} the electron, hole, excess electron and doping concentrations, respectively; and B the coefficient of radiative recombination which, in turn, itself is dependent on n and p [6, 7]. The calibration factor A_i comprises optical and geometrical properties of the investigated sample, e.g. thickness of the electrically active region, surface reflection, etc.

As can be seen in Fig. 1, a crystalline thin-film sample consists of a relatively thin epitaxial layer of the thickness W_1 and the doping concentration $N_{A,1}$ (in case of p-type dopants) on top of a substrate with the parameters W_2 and $N_{A,2}$. As always with lifetime samples, surface recombination plays an important role and should at best be minimised by an adequate surface passivation or, if this is not possible, the surface recombination velocity should at least be known, so that the measured lifetimes can be corrected appropriately. The surface recombination velocity at the front is denoted with S_1, at the back with S_2 and at the interface between epitaxial layer and substrate with S_{int}.

All samples used in this work have a highly doped p-type substrate which is chosen so for two reasons: On the one hand, a structure like this is very common with crystalline thin-film solar cells as the back contacts are located at the rear side of the substrates and the majority carriers have to flow all the way from the epitaxial base through the substrate before being collected at the back contacts. On the other hand, such a structure is also favourable for the lifetime analysis because a highly doped semiconductor material always implies a high intrinsic recombination rate and therefore a excess carrier lifetime which is limited by (intrinsic) Auger recombination. For doping concentrations $N_A > 10^{18}$ cm^{-3} e.g., the maximum excess carrier lifetime is below 10 µs. In the samples investigated, we have an even higher doping concentration of $N_{A,2}=2.6\times10^{18}$ cm^{-3}, leading to an intrinsic (Auger) limit for the maximum lifetime of 1.5 µs. This means that the fraction of excess carriers which is either generated in the substrate (that is partly the case for very thin epitaxial layers) or reaches the substrate by out-diffusion from the epitaxial layer decays rapidly there, so that the main part of the photoluminescence signal should effectively come from the epi-layer, if an epi-layer quality necessary for a sufficient solar cell performance is envisaged.

The method of extracting the epitaxial excess carrier lifetime τ_1 from the measured PL signals can best be demonstrated by a graph of the excess carrier concentration in the epitaxial layer for various layer thicknesses and carrier lifetimes in the layer. For this purpose, a Δn profile of the samples presented in this paper has been simulated with the semiconductor simulation tool PC1D [8] and is shown in Fig. 2.

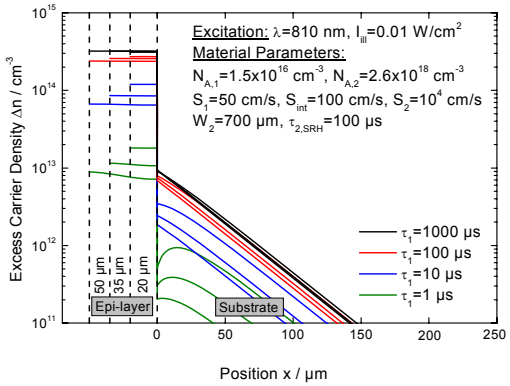

Figure 2: Excess carrier density profiles of samples with different epitaxial layer thicknesses W_1 and different epitaxial excess carrier lifetimes τ_1. The text offers more detailed information on the other parameters.

Now, if one focuses on the excess carrier density levels in the epitaxial layer, a fundamental difference between high and low lifetimes can be observed. For low lifetimes, the excess carrier concentration in the epi-layer is limited by recombination processes in the layer volume. This recombination channel is much greater than the surface recombination at the front side or the interface and also greater than out-diffusion of charge carriers into the substrate. If one assumes that all excitation light is absorbed in the epitaxial layer and that recombination and out-diffusion processes at the borders play a negligible role, then the same total amount of excess carriers have to be located in the layer volume. An epi-layer twice as thick has only half the excess carrier concentration's original value, which can indeed be seen in the upper graph. If, on the other hand, the lifetime in the epitaxial layer is very high, the recombination in the epi-layer is not limited by Shockley-Read-Hall (SRH) recombination in the volume but by recombination processes at the surfaces and out-diffusion of excess charge carriers from the layer into the substrate instead. However, these recombination processes are independent of the absolute level of carrier concentration (the assumption of approximately injection-independent surface recombination velocities should be fulfilled in the investigated range) and therefore the observed excess carrier densities have to be the same for all layer thicknesses. If one measures now the ratios of the PL intensities, which can, according to equation (1), directly be translated into a ratio of the integrated excess carrier densities, this ratio directly gives information on the lifetime in the epitaxial layer, provided that the layer thickness is known.

Therefore, the proceeding for the extraction of τ_1 is as follows: First, prepare two (or more) crystalline thin-film samples which are identical except for the epitaxial layer thickness. Second, measure the photoluminescence intensity of both samples under the same test conditions and calculate the PL intensity ratio at a fixed illumination intensity. Third, simulate the excess carrier density profile for the investigated samples and calculate the ratios of radiative recombination for several given lifetimes in the epitaxial layer. A specific calibration

curve is obtained in that way. Finally, compare the measured ratio of PL intensities with the simulated calibration curve and extract the excess carrier lifetime in the epitaxial layer.

3 SAMPLE PREPARATION

We chose to use high-purity 6" boron-doped Czochralski (Cz) wafers with a (100) orientation and a doping concentration of $N_{A,2}$=2.56×10^{18} cm^{-3} as substrates. The thickness was around W_2=700 µm and the backsides were sealed by a low-temperature oxide to prevent autodoping during the epitaxy, i.e. to prevent the out-diffusion of doping atoms from the substrate into the reaction chamber and back again into the epi-layer.

The epitaxy was realised by chemical vapour deposition (CVD) at high temperatures around 1100°C and pressures of 80 torr. The epitaxial layer always adopts the same crystal structure as the substrate surface and was also boron-doped with a doping concentration of $N_{A,1}$=1.51×10^{16} cm^{-3}. The epi-layer thickness varied between 20 µm, 35 µm and 50 µm at a very good lateral homogeneity.

After the epitaxy, the wafers were lasered into 5×5 cm^2 samples, RCA-cleaned and subsequently surface-passivated. This was done with a 70 nm SiN layer deposited by plasma-enhanced chemical vapour deposition (PECVD) at 350°C for 10 min.

4 RESULTS AND DISCUSSION

We measured the thin-film samples using the QSSPL setup described in Sect. 2. As the 6" wafers were lasered into 5×5 cm^2 pieces, 4 samples for every epi-layer thickness were available.

The LED intensity has been varied with a low frequency of 0.15 s^{-1} to ensure quasi-steady-state measurement conditions. The resulting photo-luminescence signals can be seen in Fig. 3.

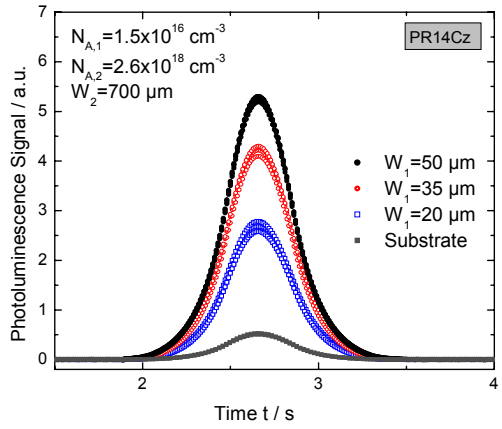

Figure 3: Measured photoluminescence signals for different crystalline silicon thin-film samples. A 1 Ωcm *p*-type epitaxial layer with thickness varying from 20 to 50 µm has been deposited on a highly doped 0.02 Ωcm *p*-type 700 µm thick silicon substrate. As can be seen, the PL signals correlate very well with the epitaxial layer thickness.

As can be seen, the PL signals correlate very well with the epitaxial layer thickness. A calculation of the PL ratios gives the value I_{50}/I_{20}=1.96 for the ratio of the measured PL intensities of the W_1=50 µm and the W_1=20 µm samples, and I_{35}/I_{20}=1.56 and I_{50}/I_{35}=1.26 for the other two combinations, respectively. The fact that the sample with the thickest epi-layer, W_1=50 µm, gives a photoluminescence signal that is nearly twice as large as in the sample with a thin epi-layer of W_1=20 µm is already a strong hint that our theoretical presumption – that most of the total photoluminescence signal comes from the epitaxial layer and only a small fraction from the substrate – is correct.

We then illuminated the samples from the substrate side. There we only measured PL intensities of I_{PL}=0.50 (same arbitrary units as in Fig. 3). Note that, in the case of illumination from the rear, the total excitation light is absorbed in the substrate and generates the measured PL light there, while in the case of illumination from the front only a small portion (depending on the epi-layer thickness) reaches the substrate. Taking the 810 nm monochromatic excitation source and its absorption length of 13 µm in silicon, one can calculate that a fraction of only 2% of the exciting light is transmitted through a 50 µm epitaxial layer. For a 35 µm or 20 µm layer this portion is still only 6% and 21%, respectively.

After having measured the PL intensities, the next step is to simulate the excess carrier profiles for different presumed epitaxial lifetimes with the aim to be able to calculate the expected ratios of radiative recombination afterwards. The result of these simulations is shown in Figure 2. As always, the final results critically depend on the specific simulation parameters, which will therefore be discussed in the following.

The doping concentration of the epitaxial layer $N_{A,1}$ was adjusted during the CVD process with an error margin of only 5%. The doping concentration of the substrate $N_{A,2}$ is given by the wafer manufacturer within the typical error margin. The substrate thickness W_2 has been determined from the finished processed sample by subtracting the epi-layer thickness from the total thickness. As stated by IMS, the lateral homogeneity as well as the absolute value of the epi-layer thickness reaches a precision of approximately 2-3% and is safely below 5%. The limiting recombination channel in the substrate is intrinsic Auger recombination which reduces the effective excess carrier lifetime in the substrate to less than 1.5 µs. SRH recombination in the substrate should not influence high-purity Cz material, even after a high-temperature CVD process. Thus the SRH lifetime is set to 100 µs as a conservative assumption.

The characteristics of the excitation source, i.e. the wavelength λ and intensity I_{ill}, have been verified in separate measurements. We also measured a variety of PL signal ratios at further illumination intensities but found that the determined photoluminescence ratios were rather robust regarding I_{ill} for these samples. This suggests an approximately injection-independent excess carrier lifetime in the investigated injection range.

Surface passivation is generally a very critical point in lifetime experiments as we intend to measure bulk recombination processes and have to exclude, or at least have to assess precisely, the influence of surface recombination. The surface recombination velocity of the front side, S_1, has been determined from simultaneously

passivated 1 Ωcm *p*-type FZ reference samples for which a value of S=23 cm/s was obtained. As we can not completely exclude additional surface influences when passivating epitaxial 1 Ωcm *p*-type material, we made a conservative S_1=50 cm/s estimate. Finally, recombination at the epitaxial layer-substrate interface has to be considered where we chose an S_{int} range from 100 to 1000 cm/s. Excess carrier profiles for both surface recombination velocity limits have been simulated.

The next step consisted of calculating the ratios of radiative recombination for several given τ_1 values by means of the simulated excess carrier density profiles. As we have shown before, the total photoluminescence signal comes almost entirely from the epitaxial layer region. Therefore, we subsequently integrated the excess carrier density over the epitaxial layer thickness region and formed the appropriate ratios. The effect of photon reabsorption [9] does not influence our analysis since all photoluminescence photons of interest exhibit the same amount of photon reabsorption.

The results can be seen as the continuous and dashed lines in Fig. 4. Note that an S_{int} value of smaller than 100 cm/s hardly has any additional effect on the final result while values considerably higher than 1000 cm/s would alter the calculated lifetimes significantly.

After having generated the so-called calibration curve, which in principle is valid for any sample with the given parameters and hence has to be calculated only once for a specific sample structure, one finally has to draw in the actually measured ratios and can then immediately determine the epitaxial layer lifetime τ_1.

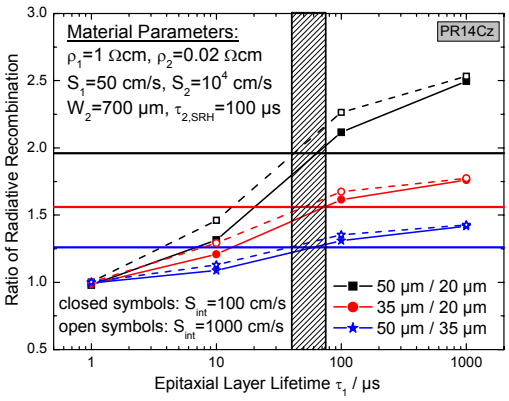

Figure 4: The calibration curve which has been calculated from the excess carrier profiles from Fig. 2 and the actually measured photoluminescence ratios are shown. If an interface recombination velocity S_{int} between 100 and 1000 cm/s is assumed, an epitaxial layer lifetime of 40 to 75 µs results.

The experimental data for all three measured PL signal ratios agree very nicely with each other, and even with an uncertainty in the interface recombination velocity S_{int} which is allowed to take any value between 100 and 1000 cm/s, the epitaxial layer lifetime is calculated to lie in a reasonably narrow range between 40 and 75 µs. Note that these excess carrier lifetimes signify diffusion lengths of 350 to 450 µm that are ten times larger than the electrically active zone and which means, from a solar cell engineering point of view, that for solar cells made from such material no limitation for the finished cell in terms of bulk recombination can be expected.

It should be stressed that the key point of the measurement and analysis principle presented here is the comparison of measured PL signal ratios with simulated radiative recombination ratios. The identity of both is only correct if the QSSPL calibration factor A_i for the two samples studied is the same and hence cancels out during calculation. However, if this is the case, the analysis method becomes a very powerful tool, as no absolute carrier lifetimes or generation profiles during the QSSPL measurement have to be determined, which is frequently a limiting requirement in conventional quasi-steady-state lifetime measurements.

5 CONCLUSION

In this study, a novel measurement and analysis method of determining the epitaxial layer lifetime in crystalline silicon thin-film samples has been presented. In principle, the concept can also be used to specify individual layer lifetimes in arbitrary multi-layer systems. It is based on the comparison between measured photoluminescence intensity ratios and simulated radiative recombination ratios. Results on epitaxial thin-film samples with varying layer thickness on a highly-doped Czochralski substrate are presented and show charge carrier lifetimes of 40 to 75 µs within the epitaxial layer.

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