Unexpectedly High Minority-Carrier Lifetimes Exceeding 20 ms Measured on 1.4-Ω cm *n*-Type Silicon Wafers

Boris A. Veith-Wolf* and Jan Schmidt

We measure very high minority-carrier lifetimes exceeding 20 ms on 1.4-Ω cm *n*-type Czochralski silicon wafers passivated using plasma-assisted atomic-layer-deposited Al_2O_3 on both wafer surfaces. The measured maximum effective lifetimes are surprisingly high as they significantly exceed the intrinsic lifetime limit previously reported in the literature. We are able to measure such high lifetimes by realizing an exceptionally homogeneous Al_2O_3 surface passivation on large-area samples (12.5 × 12.5 cm^2). The importance of the homogeneous passivation is demonstrated by comparison with samples of locally reduced passivation quality.

Very low surface recombination velocities (SRVs) have been reported for Al_2O_3-passivated *p*- and *n*-type crystalline silicon wafers.[1–8] Well-passivating Al_2O_3 layers can be deposited by various techniques[9] such as atomic layer deposition (ALD),[1–5] plasma-enhanced chemical vapor deposition (PECVD),[6,7] or even sputtering.[8] In order to obtain very low SRVs, Al_2O_3 layers deposited by plasma-assisted ALD are best suited, where SRVs below 1 cm s^{-1} have been measured on *p*-type silicon and *n*-type silicon surfaces.[3,10,11] One fundamental difference observed between Al_2O_3-passivated *p*- and *n*-type silicon surfaces was the pronounced injection-level dependence of the SRV observed on *n*-type silicon,[3] whereas the SRV was practically independent of the injection level on *p*-type silicon samples down to the lowest measured excess carrier concentrations Δn.[3,7] It was conjectured that possible damage in the space charge region during film deposition might have led to the injection dependence of the SRV at low excess carrier concentrations on Al_2O_3-passivated *n*-type silicon wafers.[11,12] However, this explanation was not consistent with the gentle nature of the ALD deposition technique applied. More recently, we suggested a different theory, which turned out to be consistent with a series of experiments.[13] The basic idea was that local regions of high recombination, e.g., at the sample edges or at scratches on the sample surface, can produce a pronounced injection dependence of the SRV on *n*-type silicon. These regions affect the SRV even at a distance due to the coupling of the regions via the inversion layer induced by the negative fixed charge density in the Al_2O_3 layer.[13] It was concluded that

local areas of reduced passivation on the surface of Al_2O_3-passivated *n*-type silicon wafers can lead to a pronounced injection dependence of the lifetime and in addition to a general decrease of the overall lifetime. Therefore, in order to be able to measure maximum lifetimes, the use of large, homogeneously passivated *n*-type silicon wafers was suggested.[13] In this paper, we verify this approach experimentally and aim at measuring thus higher lifetimes on *n*-type silicon wafers than had been measured in any study before.

We use 1.2–1.4 Ω cm *n*-type Czochralski-grown silicon (Cz-Si) wafers. The resistivity has been measured using the four-point–probe method. The wafers did not receive any special pre-treatments besides the processing described in the following. The round 6" wafers are first laser-cut into 12.5 × 12.5 cm^2 pseudo-square samples. Some samples are KOH-etched for 10 min, in order to remove the laser damage and all samples are subsequently RCA-cleaned.[14] Before KOH etching, the wafers have a thickness of (600 ± 10) μm and after KOH etching of (590 ± 10) μm. The thicknesses have been measured using a dial indicator. On both sides of the samples, a 15 nm thick Al_2O_3 layer is deposited using plasma-assisted ALD in a FlexAL^{TM} reactor (Oxford Instruments) using trimethylaluminum (TMAl) and an oxygen plasma. After Al_2O_3 deposition, which is performed at a temperature of 200 °C, the samples are annealed at 425 °C for 15 min in order to activate the Al_2O_3 passivation. Effective carrier lifetimes τ_{eff} are measured using the photoconductance decay (PCD) method (Sinton Instruments WCT120 lifetime tester). In order to collect information about the spatial distribution of the lifetime and to measure down to lower excess carrier concentrations Δn, we additionally apply the photoconductance-calibrated photoluminescence lifetime imaging (PC-PLI) method.[15]

The PC-PLI measurements show that the passivation is very homogenous and only very few areas, of limited extension, of reduced lifetime can be observed. All samples show a reduced lifetime for lower injection densities $\Delta n < 10^{14}$ cm^{-3}, especially close to the edge, due to the above-mentioned edge recombination effect.[13] We measure the highest lifetime on a 1.4-Ω cm KOH-etched *n*-type sample with a maximal lifetime of 24.1 ms (at $\Delta n = 1.3 \times 10^{14}$ cm^{-3}) measured using PC-PLI and 23.7 ms (at $\Delta n = 1.9 \times 10^{14}$ cm^{-3}) measured using PCD, as can be seen in **Figure 1**. This lifetime is, to our knowledge, hitherto the highest reported lifetime for crystalline *n*-type silicon with a resistivity of around 1 Ω cm. This lifetime is well above the commonly used intrinsic limit by Richter et al.,[10] which is 17 ms

B. A. Veith-Wolf, Prof. J. Schmidt
Institute for Solar Energy Research Hamelin (ISFH), Am Ohrberg 1, 31860 Emmerthal, Germany
E-mail: b.veith-wolf@isfh.de

Prof. J. Schmidt
Department of Solar Energy, Institute of Solid-State Physics, Leibniz Universität Hannover, Appelstrasse 2, 30167 Hannover, Germany
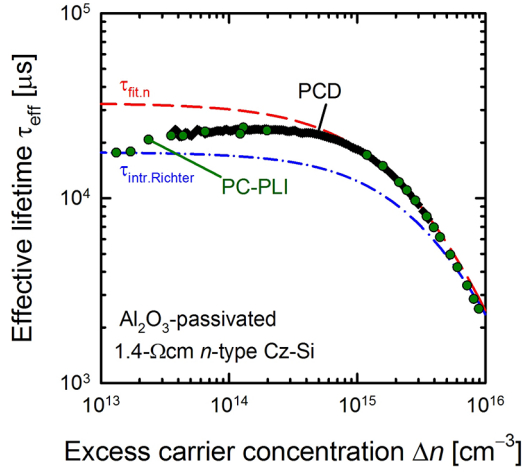
Figure 1. Effective lifetime τ_{eff} measured using PCD (diamonds) and PC-PLI (circles) as a function of the excess carrier concentration Δn of a 590 µm thick 1.4-Ω cm n-type Cz-Si sample passivated with 15 nm Al$_2$O$_3$ on both surfaces. Also shown is the intrinsic lifetime parameterization by Richter et al.[10] (dash-dotted line) and our fitted lifetime according to Eq. (2) (dashed line).

(at $\Delta n = 1 \times 10^{14}\,\text{cm}^{-3}$). Therefore, an adapted parameterization of the intrinsic lifetime for n-type silicon seems to be necessary. This is also supported by publications of Wan et al.[16] and Niewelt et al.[17] who measured lifetimes exceeding the intrinsic limit by Richter et al. on n-type float-zone silicon.

Within the past two decades, the parameterization of the intrinsic lifetime in crystalline silicon was adapted several times. The most widely used parameterization was published by Kerr and Cuevas.[18] However, with the later improvements in the surface passivation quality, especially the introduction of the excellent Al$_2$O$_3$ passivation, a new parameterization was developed by Richter et al.[10] This parameterization is based on lifetime measurement on n- and p-type silicon samples passivated with Al$_2$O$_3$. In Richter's study, small-area samples were predominantly used. In the case of n-type silicon samples, the measured lifetimes might have been subject to the above-mentioned effects of the coupling of low-lifetime regions (such as edges and scratches) to high-lifetime regions via the Al$_2$O$_3$-induced inversion layer. Hence, all lifetimes used in the Richter parameterization[10] for n-type silicon in the resistivity range of 1–2 Ω cm were well below the lifetimes we measure in this study on large-area wafers of homogeneous passivation quality.

In order to allow for advanced device simulations, we perform here a fit of our lifetime data. In order to generate this fit, we follow the basic approach of Kerr and Cuevas[18] and use for n-type crystalline silicon the equation

$$\tau_{\text{fit.n}} = \frac{\Delta n}{np\left(g_{\text{eeh}}(n_0) \cdot C_n \cdot n_o + g_{\Delta n}(\Delta n) \cdot C_a \cdot \Delta n + B\right)}, \quad (1)$$

with the radiative recombination coefficient $B = 4.73 \times 10^{-15}\,\text{cm}^3\,\text{s}^{-1}$,[19] the Auger coefficient of the electron–electron–hole process $C_n = 2.8 \times 10^{-31}\,\text{cm}^6\,\text{s}^{-1}$,[20] and g_{eeh} and $g_{\Delta n}$ being empirical Coulomb-enhancement factors,[18] which we fit to our

injection-dependent lifetime measurements at a fixed doping concentration of $n_0 = 3.5 \times 10^{15}\,\text{cm}^{-3}$. For the ambipolar Auger coefficient C_a different values can be found in the literature, for a good overview see for example Kerr and Cuevas.[18] Most reported values are in the range of $(1–2) \times 10^{-30}\,\text{cm}^6\,\text{s}^{-1}$, hence, we use $C_a = 1.5 \times 10^{-30}\,\text{cm}^6\,\text{s}^{-1}$ in our fit. In order to extend the fit of the injection-dependent lifetime also to Δn values larger than the measured injection range, i.e., for $\Delta n > 10^{16}\,\text{cm}^{-3}$, we use the Richter parameterization as a "boundary condition". This can be done because the lifetime measurements at $\Delta n > 10^{16}\,\text{cm}^{-3}$ are not influenced by the edge recombination effect[13] and hence the Richter parameterization is valid in this regime. This "boundary condition" is employed by minimizing the deviation of our fitted lifetime $\tau_{\text{fit.n}}(\Delta n)$ from the Richter lifetime $\tau_{\text{intr.Richter}}$ for Δn values between 10^{16} and $10^{17}\,\text{cm}^{-3}$.

In order to extract the exact bulk lifetime from the measured effective lifetime, the knowledge of the surface recombination velocity is required, however, since the passivation of n-type silicon with Al$_2$O$_3$ leads to SRVs below $1\,\text{cm}\,\text{s}^{-1}$, we neglect the SRV and use instead the approximation that the bulk lifetime is larger than the measured effective lifetime. For SRVs below $0.3\,\text{cm}\,\text{s}^{-1}$,[10] this assumption leads to an underestimation of the bulk lifetime that is smaller than 20%. Simulations using Sentaurus Device with the model described in Ref. [13] show that even if assuming completely negligible surface recombination, the lifetime below $\Delta n = 10^{15}\,\text{cm}^{-3}$ is reduced due to the edge recombination effect.[13] Therefore, only the measured lifetimes at $\Delta n > 10^{15}\,\text{cm}^{-3}$ are taken into account and the following fit is obtained ($\tau_{\text{fit.n}}$ in seconds and concentrations in cm^{-3}):

$$\tau_{\text{fit.n}} = \frac{\Delta n}{np\left(4 \times 10^{-15} + 7.7 \times 10^{-28}\Delta n^{0.84} + B\right)}. \quad (2)$$

The deviation of $\tau_{\text{fit.n}}$ from $\tau_{\text{intr.Richter}}$ for Δn values between 10^{16} and $10^{17}\,\text{cm}^{-3}$ is smaller than 10%. Since we neglect the surface recombination, this fit should be regarded as lower boundary.

To come as close to the intrinsic lifetime as possible with the measured effective lifetimes, an outstanding homogeneity of the surface passivation is crucial. In our experiment, we processed several wafers and not all of them showed maximum lifetimes. **Figure 2** shows PC-PLI measurements of two different 1.3-Ω cm n-type Cz-Si samples passivated with Al$_2$O$_3$ on both surfaces. The injection-dependent lifetime is very different for these two samples, resulting in a lower maximum lifetime measured in the wafer center of 11 ms for sample B compared to 22 ms for sample A. The difference between the measured lifetimes of these two samples might be due to the scratch in the lower right corner on the surface of sample B. We also observe a reduction of the lifetime after several measurements, due to scratches from the handling. Hence, n-type samples passivated with Al$_2$O$_3$ are very sensitive to scratches induced by the handling. Therefore, the use of a capping layer, e.g., SiN$_x$, needs to be evaluated in order to be able to perform several repeated measurements on the same sample.

We have measured lifetimes on n-type Cz-Si wafers passivated with Al$_2$O$_3$ well above the intrinsic lifetime limit calculated using the frequently used lifetime parameterization by Richter et al.[10]
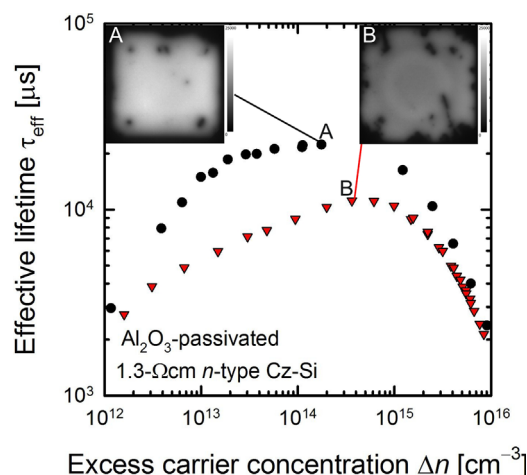
ADVANCED
SCIENCE NEWS

www.advancedsciencenews.com

physica
status
solidi
pss rrl

www.pss-rapid.com

Figure 2. Area-averaged effective lifetime τ_{eff} as a function of excess carrier concentration Δn measured using photoluminescence imaging. Shown are the results for 1.3-Ω cm n-type Cz-Si samples passivated with 15 nm Al_2O_3 on both surfaces. One sample shows a less homogeneous passivation (triangles) leading to an overall lifetime reduction compared to the homogeneously passivated sample (circles). The lifetime is extracted from the center of the sample using a circle with a diameter of 2 cm. In the insets, the PC-PLI images for the highest lifetimes, marked with the line, for each sample are shown.

It is therefore obvious that an adapted parameterization for n-type silicon is required. We have presented a fit to the measured injection-dependent lifetime as a starting point for further investigations. In order to develop a complete parameterization of the intrinsic lifetime, silicon wafers passivated with Al_2O_3 are very well suited, however, the preparation of the samples is extremely sensitive to local inhomogeneities in the surface passivation quality. We have demonstrated that already small areas of reduced passivation quality might lead to a strong reduction in the overall effective lifetime and also to an increased injection dependence. In order to develop a complete improved lifetime parameterization for n-type crystalline silicon, we are planning to carry out lifetime measurements with the methodology outlined in this letter for n-type silicon wafers of various resistivities. Note that the fact that the intrinsic lifetime in n-type silicon had been underestimated in previous studies has also a direct impact on the maximum achievable efficiency of solar cells fabricated on n-type silicon wafers, which is therefore higher than previously assumed.

Acknowledgment

Conflict of Interest

The authors declare no conflict of interest.

Keywords

[1] G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H. F. W. Dekkers, S. De Wolf, G. Beaucarne, Sol. Energy Mater. Sol. Cells 2006, 90, 3438.

[2] B. Hoex, S. B. S. Heil, E. Langereis, M. C. M. van de Sanden, W. M. M. Kessels, Appl. Phys. Lett. 2006, 89, 042112.

[3] B. Hoex, J. Schmidt, P. Pohl, M. C. M. van de Sanden, W. M. M. Kessels, J. Appl. Phys. 2008, 104, 044903.

[4] J. Benick, A. Richter, M. Hermle, S. W. Glunz, Phys. Status Solidi RRL 2009, 3, 233.

[5] F. Werner, B. Veith, D. Zielke, L. Kühnemund, C. Tegenkamp, M. Seibt, R. Brendel, J. Schmidt, J. Appl. Phys. 2011, 109, 113701.

[6] P. Saint-Cast, D. Kania, M. Hofmann, J. Benick, J. Rentsch, R. Preu, Appl. Phys. Lett. 2009, 95, 151502.

[7] B. Veith, T. Dullweber, M. Siebert, C. Kranz, F. Werner, N.-P. Harder, J. Schmidt, B. F. P. Roos, T. Dippell, R. Brendel, Energy Proc. 2012, 27, 379.

[8] T.-T. A. Li, A. Cuevas, Phys. Status Solidi RRL 2009, 3, 160.

[9] J. Schmidt, F. Werner, B. Veith, D. Zielke, R. Bock, V. Tiba, P. Poodt, F. Roozeboom, A. Li, A. Cuevas, R. Brendel, in Proceedings of the 25th European Photovoltaic Solar Energy Conference, Valencia, Spain, 2010 (WIP, Munich, Germany, 2010), pp. 1130–1133.

[10] A. Richter, S. W. Glunz, F. Werner, J. Schmidt, A. Cuevas, Phys. Rev. B 2012, 86, 165202.

[11] F. Werner, A. Cosceev, J. Schmidt, J. Appl. Phys. 2012, 111, 073710.

[12] S. Steingrube, P. P. Altermatt, D. Zielke, F. Werner, J. Schmidt, R. Brendel, in Proceedings of the 25th European Photovoltaic Solar Energy Conference, Valencia, Spain, 2010 (WIP, Munich, Germany, 2010), pp. 1748–1754.

[13] B. Veith, T. Ohrdes, F. Werner, R. Brendel, P. P. Altermatt, N.-P. Harder, J. Schmidt, Sol. Energy Mater. Sol. Cells 2014, 120, 436.

[14] W. Kern, J. Electrochem. Soc. 1990, 137, 1887.

[15] S. Herlufsen, J. Schmidt, D. Hinken, K. Bothe, R. Brendel, Phys. Status Solidi RRL 2008, 2, 245.

[16] Y. Wan, K. R. McIntosh, A. F. Thomson, A. Cuevas, in Proceedings of the 38th IEEE Photovoltaic Specialists Conference, Austin, TX, USA, 2012, Part 2 (IEEE, New York, USA, 2012), pp. 1–7.

[17] T. Niewelt, W. M. Kwapil, M. Selinger, A. Richter, M. C. Schubert, IEEE J. Photovolt. 2017, 7, 1197.

[18] M. J. Kerr, A. Cuevas, J. Appl. Phys. 2002, 91, 2473.

[19] T. Trupke, M. A. Green, P. Würfel, P. P. Altermatt, A. Wang, J. Zhao, R. Corkish, J. Appl. Phys. 2003, 94, 4930.

[20] J. Dziewior, W. Schmid, Appl. Phys. Lett. 1977, 31, 346.