Development of recombination lifetime measurement methods for photovoltaic applications

Ph.D. Thesis booklet

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Introduction

The continuous development of solar cells over the past decades has resulted in a dynamic year-on-year increase in their contribution to global energy production. In 2023, solar energy became the leading source of newly installed energy capacity globally [1]. These achievements have been made possible by decades of research and development in materials science and semiconductor technology. The current record for photoelectric conversion efficiency in silicon-based single-junction solar cells is 27.3% [2], which approaches the recently updated theoretical efficiency limit 29.4% [3, 4]. This limit considers the inevitable losses beyond the well-known Shockley-Queisser limit [5]. Therefore, any further enhancement necessitates an even more precise determination of the relevant physical parameters. Another significant trend is the shrinking gap between record efficiencies achieved in R&D laboratories and the efficiencies of solar cells manufactured on modern production lines [6]. Consequently, advanced and more accurate measurements are needed not only to achieve further efficiency records but also to reliably control manufacturing processes.

In solar cells, a dominant factor determining the performance is the recombination rate of excess charge carriers. The bulk recombination rate within a silicon wafer, governed by the initial crystal quality and the concentration of defects and impurities, plays a central role in determining the solar cell efficiency. Additionally, surface recombination, occurring at the p-n junction and near ohmic contacts, becomes a critical factor for solar cell devices as well. To further increase energy conversion efficiency, the reduction of recombination-related energy losses is a primary goal of research projects. For this purpose, the optimization of the Czochralski process for pulling monocrystalline silicon material [7–10] and the development of complex solar cell structures [11–15] are ongoing research topics.

Objectives

Understanding and quantifying the recombination properties of silicon is essential for improving the performance of solar cells. A wide variety of measurement methods have been developed for the precise determination of charge carrier recombination lifetime. Compliance with modern manufacturing requirements demands the use of fast and non-contact technologies. Therefore, the most common measurement solutions currently rely on optical excitation and contactless detection sensitive to excess carriers. Commercial measurement systems utilize microwave reflectance [16, 17] or radio-frequency eddy-current sensors [18, 19] for this purpose.

This work focuses on the development and applications of recombination lifetime measurement methods, primarily for the investigation of solar cell materials and structures, for both industrial quality control and research purposes. I believe that my work over the past four years has made a significant contribution to the photovoltaic research community and industry at three distinct levels.

At the Budapest University of Technology and Economics (BME), my research group determined the recombination properties of novel photovoltaic materials [20] (in the perovskite family) using cryogenic carrier lifetime measurement systems, recording the recombination properties as a function of temperature [21, 22]. Recognizing the nonlinear behavior of the system, I developed a novel self-consistent calibration method. Beyond the development of the applied evaluation routines, I devised a method to verify the reliability of measurements over the entire investigated temperature range.

My work at Semilab Semiconductor Physics Laboratory Co. Ltd. (Semilab) has enabled the experimental determination of excess carrier lifetime in silicon samples used in different phases of solar cell manufacturing process. First, I re-newed a carrier lifetime measurement technique and established an iterative, simulation-based evaluation method to precisely determine the bulk carrier lifetime of thick silicon samples. This enabled to investigate the bulk recombination processes of very high-quality silicon ingots which is not possible in other ways.

I developed a unique measurement method combining, for the first time, three independent carrier lifetime measurement principles for the investigation of passivated silicon wafers. This method enabled the simultaneous determination of the density, the lifetime and the mobility of excess charge carriers in modern silicon-based solar cell structures with unprecedented accuracy. This technique is particularly important for the investigation non-standard wafer types with unknown material parameters, or modern solar cell structures with highly conductive surface layers, which pose challenges in determining carrier lifetime.

Application of the developments

I carried out my work within the framework of a university-industry collaboration, so my research and development results were utilized in both the scientific field and industrial applications.

The novel, self-consistent calibration method can be universally applied to study recombination in novel materials, thereby contributing to a better understanding of charge carrier dynamics in perovskite crystals in the ongoing research at BME.

The simulation-assisted evaluation developed for the investigation of thick silicon samples is already applied in commercial carrier lifetime measurement systems, providing rapid and precise information about possible contamination in an early production phase. My results contributed to enhance the reliability of quality control. Furthermore, it is the first method capable of characterizing actual bulk recombination processes in very high-quality silicon ingots without the distortion of surface recombination. Both industrial and R&D projects are ongoing to exploit this feature of the method.

The combined measurement technique for passivated silicon wafers enables determining the carrier lifetime versus injection level with unprecedented precision. This allows for the precise predictions of the solar cell voltage prior to contact formation (eliminating the $5-10\,\mathrm{mV}$ uncertainty that has existed so far using standard methods). Furthermore, this technique enables carrier mobility measurements providing important information for rather exotic materials, where existing mobility models are not valid. The potential of this method is being further explored through ongoing international collaboration projects.

My findings have already triggered superimposed researches. By modifying the combined carrier lifetime experimental setup, temperature-dependent carrier lifetime curves were recorded, leading to a successful MSc thesis by Gergely Havasi under my supervision.

Thesis points

1. I developed a self-consistent calibration method for a research-grade microwave-detected photoconductance decay measurement setup. This method is independent of the sample and the illumination spot size. I validated the method by measuring silicon wafers with different thicknesses and bare surface, where the measurable lifetime is limited by the diffusion process of charge carriers. This test also enabled to determine the low injection mobility of minority charge carriers down to $120\,\mathrm{K}$. [T1]

2. I have conducted a detailed investigation into the time-dependent behavior of surface recombination during photoconductance decay (PCD) measurements on thick silicon samples. I found that the distorting effect of the surface recombination on the measurement continuously diminishes during the decay of excess charge carrier density. I explored the severity of the surface recombination related distortions as a function of the wavelength of the optical excitation. Based on this analysis, I determined that the optimal wavelength range for characterizing thick silicon samples by PCD methods lies between $1050-1070\,\mathrm{nm}$. I investigated

the depth sensitivity of eddy-current-based measurements in the presence of inhomogeneous carrier distributions. This led to a phenomenological model that offers sufficient accuracy for practical applications. Charge carrier simulations and surface passivation experimental tests led to consistent results. The discrepancy between the measurable effective lifetime and the reference bulk lifetime value at the industrial standard $10^{15}\,\mathrm{cm}^{-3}$ injection level is below 20% without using corrections of the surface recombination phenomena. [T2]

3. I developed a complex simulation method of the photoconductance decay (PCD) measurement of thick silicon slugs considering the charge carrier dynamics and the depth sensitivity of the eddy current sensor as well. I reconstructed the bulk lifetime from the measured decay curves using this simulation iteratively. This way I created a new evaluation method including the correction of surface recombination and the inhomogeneous depth sensitivity. I tested the method on p-type photovoltaic silicon samples, and found a very good agreement between the evaluated bulk lifetime and the lifetime results measured on well-passivated neighboring wafers. Measurements on n-type samples in the transitional thickness range also confirmed the accuracy of the method. This way, I characterized such samples in this early production phase with outstanding accuracy. [T3]

4. I integrated the photoconductance decay (PCD) and the small perturbation photoconductance decay (SP-PCD) carrier lifetime measurement methods into one measurement setup. These techniques complement each other for accurate measurement in terms of injection level ranges. Therefore, their combination allows the investigation of passivated silicon wafers in a wide injection level range ($10^{13}\,\mathrm{cm}^{-3} - 10^{17}\,\mathrm{cm}^{-3}$). This self-consistent method does not require the exact knowledge of the optical properties of the sample and carrier mobility data. I investigated the injection-dependent lifetime of high quality silicon wafer structures used for modern solar cell types with the highest theoretically possible accuracy. [T4]

5. I realized steady-state photoconductance (SS-PC) carrier lifetime measurements on silicon wafers by complementing the measurement setup with a temperature stabilization method. Combining this technique with the transient PC measurement, I determined the charge carrier mobility of crystalline silicon in p- and n-type solar cell structures as well with higher accuracy than earlier studies, which applied less sophisticated methods. I compared the mobility results to accepted and widespread injection-dependent mobility models. [T5]

List of Publications

[T1] D. Krisztian *et al.*, "Novel calibration method for mw-pcd measurement," *in preparation*, 2025.

[T2] D. Krisztian, F. Korsos, I. Saegh, G. Parada, M. Kovács, Z. Verdon, C. Jobbágy, P. Tüttő, X. Dong, H. Deng, S. Wang, and X. Chen, "Improved accuracy of eddy-current sensor based carrier lifetime measurement using laser excitation," *EPJ Photovoltaics*, vol. 13, p. 3, 01 2022.

[T3] D. Krisztian *et al.*, "Determination of bulk carrier lifetime of silicon ingots using iterative simulation-base evaluation of pcd measurement," *in preparation*, 2025.

[T4] D. Krisztian, F. Korsos, E. Kis, G. Parada, and P. Tüttő, "Integrated measurement of the actual and small perturbation lifetimes with improved accuracy," *AIP Conference Proceedings*, p. 110005, 01 2023.

[T5] D. Krisztian, F. Korsos, and G. Havasi, "Simultaneous measurement of charge carrier concentration, mobility, and lifetime," *Solar Energy Materials and Solar Cells*, vol. 260, p. 112461, 09 2023.

Other publications not included as thesis points

1. B. Sánta, Z. Balogh, A. Gubicza, L. Pósa, D. Krisztián, Gy. Mihály, M. Csontos, A. Halbritter, *Universal 1/f type current noise of Ag filaments in redox-based memristive nanojunctions*. Nanoscale, 11, 10.1039/C8NR09985E (2019)

2. B. Sánta, Z. Balogh, L. Pósa, D. Krisztián, T. Török, D. Molnár, Cs. Sinkó, R. Hauert, M. Csontos, A. Halbritter, *Noise Tailoring in Memristive Filaments*. ACS applied materials & interfaces, 10.1021/acsami.0c21156 (2021)

3. L. Pósa, Z. Balogh, D. Krisztián, P. Balázs, B. Sánta, R. Furrer, M. Csontos, A. Halbritter, *Noise diagnostics of graphene interconnects for atomic-scale electronics*. npj 2D Materials and Applications, 5. 57. (2021)

4. A. Bojtor, D. Krisztián, F. Korsós, S. Kollarics, G. Paráda, T. Pinel, M. Kollár, E. Horváth, X. Mettan, H. Shiozawa, B. Márkus, L. Forró, F. Simon, *Millisecond-Scale Charge-Carrier Recombination Dynamics in*

the $CsPbBr_3$ Perovskite. Advanced Energy and Sustainability Research, 5. 10.1002/aesr.202400043 (2024)

5. A. Bojtor, D. Krisztián, F. Korsós, S. Kollarics, G. Paráda, M. Kollár, E. Horváth, X. Mettan, B. Márkus, L. Forró, F. Simon, *Dynamics of Photoinduced Charge Carriers in Metal-Halide Perovskites*. Nanomaterials, 14. 1742. 10.3390/nano14211742 (2024)

6. A. Bojtor, D. Krisztián, G. Paráda, F. Korsós, S. Kollarics, G. Csősz, B. Márkus, L. Forró, F. Simon, *A Versatile System for Photoconductance Decay Measurement Across a Wide Range of Semiconductor Materials*. 10.48550/arXiv.2411.16892. (2024)

7. G. Havasi, D. Krisztián, F. Korsós, S. Fu, *Implied J-V Curves Recorded at Elevated Temperatures Using Light Controlled Heating*. SiliconPV Conference Proceedings, 2. 10.52825/siliconpv.v2i.1336 (2024)

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