Presented at the 29th European PV Solar Energy Conference and Exhibition, 22-26 September 2014, Amsterdam, The Netherlands

INLINE QUALITY CONTROL OF PASSIVATION STACKS IN HIGH-EFFICIENCY SILICON SOLAR CELL CONCEPTS: THICKNESS DETERMINATION FROM SPECTRO-PHOTOMETRY

Johannes Greulich, Nico Wöhrle, Alexander Krieg, Stefan Rein
Fraunhofer Institute for Solar Energy Systems
Heidenhofstr. 2, D-79110 Freiburg, Germany
Phone: +49 761 4588 5488. Fax: +49 761 4588 7621. E-mail: johannes.greulich@ise.fraunhofer.de

ABSTRACT: Stacks of dielectric thin films are widely used for passivated emitter and rear solar cells based on crystalline silicon. The film thicknesses influence both the electrical and optical properties of these devices. The standard offline method for the optical characterization of these films is ellipsometry. Since the spectral reflectance of solar cells and precursors can be measured inline using spectro-photometry, we evaluate a method for the determination of the passivation layer thicknesses from spectral reflectance data in the UV-Vis and compare it to ellipsometric offline-measurements. The crucial point is to exploit the whole reflectance spectrum instead of utilizing only a single wavelength where a reflectance minimum occurs. It is shown that comparable film thicknesses can be determined from both spectro-photometry and ellipsometry. Furthermore, spectro-photometry is more robust on rough samples. Even film thicknesses below 30 nm can be determined if the reflectance data extends to the ultraviolet part of the spectrum.
Keywords: characterisation, optical properties, passivation, thin film

1 INTRODUCTION

One rather conservative route to higher energy conversion efficiencies of silicon solar cells is the passivated emitter and rear cell (PERC) concept [1], applying a dielectric passivation of the rear surface combined with local contacts [2]. This approach is therefore currently being adapted in the industrial production. The thickness of the rear passivation layers influences both the electrical and optical properties of these devices. The standard offline method to characterize the optical properties of such films is in case of planar surfaces ellipsometry, but also the spectral reflectance can be used to determine the film thickness [3]. However, ellipsometry is intricate and error-prone on rough surfaces due to depolarization and low signal intensities [4, 5]. Since the measurement of the reflectance is more robust and available inline, we focus on this technique for the inline quality control of passivation stacks in PERC cells.

Several approaches to characterize thin films based on reflectance or transmittance spectra have been evaluated in the past. Sopori suggests to use a reflectometer to determine the thickness $d=\lambda_0/4/n$ of a single dielectric thin film on silicon using the wavelength λ_0 of the reflectance minimum and the refractive index n of the thin film [6]. Dobrowolski *et al.* apply a least-squares fit of the optical constants of a single thin film to the measured spectral reflectance $R(\lambda)$ and transmittance $T(\lambda)$, but do not determine the film thickness [7]. Ylilammi and Ranta-aho used the Sellmeier-equation for the optical constants, which are determined along with the film thickness of single thin films from $T(\lambda)$. For multilayers, they use fixed optical constants and fit the layer thicknesses to $T(\lambda)$ [8]. Sreemany and Sen did a similar analysis fitting $n(\lambda)$ and d to reflectance and transmission spectra of single thin films on transparent substrates [9].

In the present work, we evaluate a similar approach. The spectral hemispherical reflectance $R(\lambda)$ of the rear surface of PERC precursors coated with a double layer passivation stack is analyzed in order to determine the thickness of the thin films. The refractive indices of the materials are assumed to be known and constant. This approach is compared to spectral and laser ellipsometry for a variety of film thicknesses. First, in section 2 the theory underlying the approach is described. In section 3, the preparation of the samples, the measurement

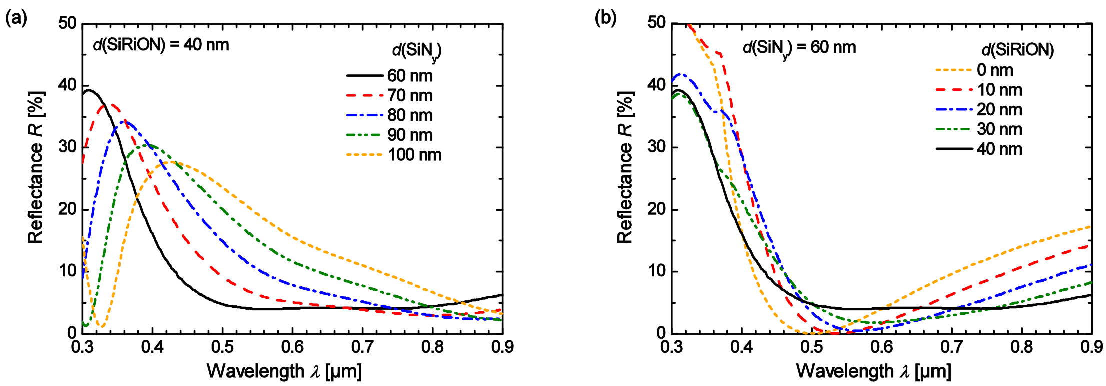

Figure 1: Exemplary reflectance spectra for (a) constant SiRiON thickness (40 nm) and varied SiN_y thickness (60 – 100nm) and (b) constant SiN_y thickness (60 nm) and varied SiRiON thickness (0 – 40 nm). The refractive index of SiRiON and SiN_y is approximately 3.2 and 2.1 at 600 nm, respectively (see Figure 2).

instruments and the measurement results are described. The results are discussed in section 4. The conclusions can be found in section 5.

2 THEORY

In the UV-Vis spectral range, the spectral reflectance *R(λ)* of a silicon wafer coated with two thin films depends only on the complex refractive index of silicon $n_s(\lambda)$ and the two thin films $n_1(\lambda)$ and $n_2(\lambda)$, and on the films' thicknesses d_1 and d_2. An expression of the functional relationship is derived using the transfer matrix algorithm [10] and the reflectance is calculable for any given film thicknesses and refractive indices. If the refractive indices are known and kept constant, the computed spectral reflectance

$$R_{\text{com}} = R_{\text{com}}(\lambda, d_1, d_2) \tag{1}$$

depends only on the film thicknesses. Selected computed reflectance spectra for a stack consisting of SiN_y and silicon-rich silicon oxy-nitride (SiRiON, [11]) on planar silicon are shown in Figure 1 for a variety of film thicknesses. For the thin films, the refractive indices shown in Figure 2 are used and for the silicon wafer, those given in Ref. [12]. It is apparent that film thicknesses as thin as 10 nm already change the shape of the reflectance spectrum significantly. This fact is intended to be exploited in the following paper.

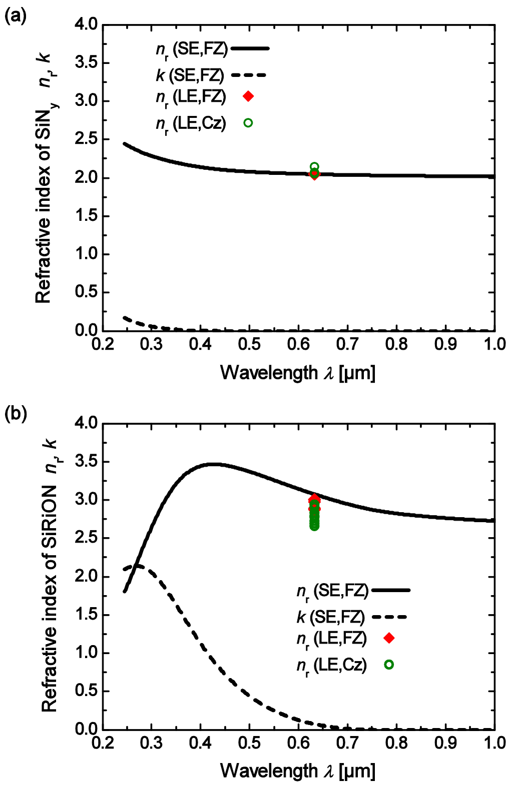

Figure 2: (a) The spectral refractive index of SiN_y as measured with a spectral ellipsometer (SE) on planar FZ reference samples and with a laser ellipsometer (LE) on planar FZ wafers and slightly rough Cz samples. (b) The spectral refractive index of SiRiON as measured with a spectral ellipsometer (SE) on planar FZ reference samples and with a laser ellipsometer (LE) on planar FZ wafers and slightly rough Cz samples.

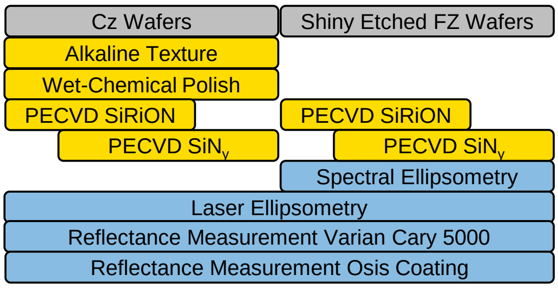

Figure 3: The flow chart gives an overview of the process steps (yellow) and the characterization steps (blue) for both the Cz and the FZ samples.

In the present approach, expression (1) is compared to the spectral reflectance $R_{\text{meas}}(\lambda)$ of PERC precursors, measured right before metallization. The film thicknesses are then adjusted with a Python script [13, 14] using a non-linear least-squares algorithm [15, 16] to fit the computed to the measured reflectance.

3 RESULTS

3.1 Sample preparation

The following samples are prepared as basis for the evaluation of the fit algorithm. The process and characterization sequence of the batch are summarized in Figure 3. This batch comprises two types of samples. Shiny etched, 200 µm thick, *p*-type float-zone (FZ) wafers with very planar surfaces (RMS roughness < 50 nm) are intended as reference system. PERC-like samples made of Czochralski (Cz) grown wafers with a process sequence similar to a possible process sequence of PERCs serve to evaluate the approach on a realistic set of samples. These samples were textured with random pyramids on both sides using potassium hydroxide base and were subsequently single-side polished [17] using a combination of hydrofluoric acid and nitric acid resulting in an irregular, slightly rough rear surface with RMS roughness of 1 µm.

The rear surfaces are coated with a dual layer passivation stack consisting of silicon-rich silicon oxy-nitride (SiRiON) and silicon nitride (SiN_y) [11] of varying thickness via PECVD using the SiNA-tool from Roth & Rau. The nominal thickness of the SiRiON layer is 20 nm, 30 nm and 40 nm, whereas the nominal thickness of the SiN_y is 60 nm, 80 nm and 100 nm. Combining each SiRiON-thickness variant with each SiN_y-thickness variant yields nominally nine different stacks. Each individual stack is deposited on six Cz samples and on three FZ wafers in order to check the repeatability. Due to an error during PECVD the group of FZ wafers with the stack of 20 nm SiRiON and 100 nm SiN_y is lost. The true thicknesses of the layers deviate from the nominal thicknesses by few nanometers due to process inhomogeneity. Besides these dual layer samples, also reference samples with only one layer are manufactured. For each single layer and nominal thickness, three Cz and two FZ wafers are prepared.

3.2 Determination of the refractive indices

On the single-layer FZ samples the dispersion of the refractive indices $n_{1/2}(\lambda)$ and $k_{1/2}(\lambda)$ is measured with a spectral ellipsometer from J.A. Woollam Inc., type M-2000F. Due to depolarization and low signal intensities, we were not able to measure the refractive indices on the slightly rough Cz samples with this spectral ellipsometer. The measurements are done combining three different angles (65°, 70°, 75°) of the incident light. The determination of the refractive indices is based on a fit of the Tauc-Lorentz model [18]. According to a recent examination ([19], p. 83), a 0.8 nm thin native oxide layer is assumed, too.

With a Sentech SE 400 adv laser ellipsometer working at about 633 nm, the layer thickness and the real part of the refractive index $n_r(\lambda = 633\text{ nm})$ of the SiN_y and the SiRiON layer are determined on the FZ single-layer samples and the Cz single-layer samples for comparison. Here as well, a 0.8 nm thin native oxide layer is assumed.

The spectral ellipsometry data show that SiN_y is weakly absorbing having a weak dispersion around $n_r(SiN_y) \approx 2.05$ (see Figure 2a). The laser ellipsometry confirms the spectral measurements. Perfect agreement of both tools concerning $n_r(SiN_y)$ is found for all samples. Even the measurement on the slightly rough Cz-samples with the thickest SiN_y layer deviates only slightly by less than $\Delta n_r \approx +0.01$. The SiRiON shows a higher extinction and has a rather strong dispersion in the range of $0.25\ \mu m < \lambda < 1.0\ \mu m$ with $1.7 < n_r(\text{SiRiON}) < 3.5$ (see Figure 2b). The measurements with the laser ellipsometer roughly confirm the spectral measurements, although for some of the Cz samples, a slight spread of the data is observed, in this case by $\Delta n_r \approx -0.4$. This apparent spread is attributed to the artifacts induced by the rough wafer surface, not to an actual change of the refractive index since the PECVD process was identical for all samples.

3.3 Ellipsometric determination of the layer thicknesses

The thickness of the SiN_y and SiRiON films on the FZ and on the Cz samples is determined with laser and spectral ellipsometry for both single- and double-layer systems. The layer thicknesses determined with the ellipsometers are used as reference for the fit of the spectral reflectance analyzed in sections 3.4 and 3.5.

As can be seen in Figure 5, on the FZ samples, the measurements with the spectral ellipsometer show that the measured SiN_y thickness agrees within 5 nm with the nominal thickness on the single- and double-layer samples. The SiRiON thickness is measured with the spectral ellipsometer up to 12 nm thicker than the intended thickness, both in the stack and as single layer. The deviations are rather small for thin SiRiON layers and rather large for thick SiRiON layers indicating that the deposition took place faster than intended. The spectral ellipsometer fails on the rough Cz samples, probably due to scattering and depolarization of the incident white light.

In case of the laser ellipsometer, the refractive indices as determined with the spectral ellipsometer on the single layer samples are used in order to determine the film thicknesses. As shown in Figure 5, the measurements on the planar FZ samples coated with single layers agree within 2 nm (5 nm) with the results of the spectral ellipsometer for the SiN_y (SiRiON) layers. However, within the stack, the determined thickness of the SiN_y layer apparently decreases continuously by up to 20 nm as the SiRiON thickness increases (Figure 5, lower half), although all wafers with the same SiN_y thickness were coated within the same run, which makes such large thickness variations very unlikely. On the Cz samples, the measurements show a similar characteristic as on the FZ samples as shown in Figure 6. Significant differences in the deposition of the dielectrics on planar and rough surfaces are therefore excluded.

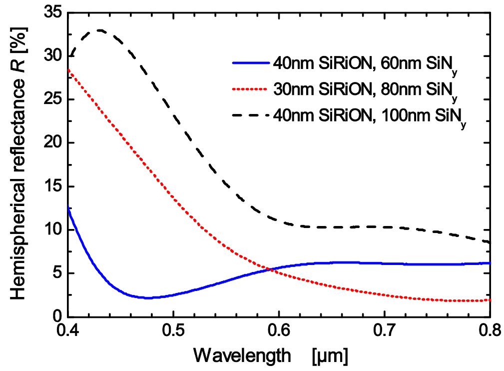

Figure 4: The reflectance spectra measured with the high-precision spectro-photometer (Varian Cary 5000) and with the multichannel CCD-spectrometer (OP-tection Osis Coating, averaged values) match closely for the exemplarily shown FZ-samples with the layer thicknesses indicated in the legend.

3.4 Measuring the reflectance

The spectral hemispherical reflectance of all samples is measured on the wet-chemically polished side with an UV-VIS-NIR spectral photometer of type Cary-5000 and an integrating Ulbricht sphere of the company Varian. Besides, the spectral diffuse reflectance is measured at selected Cz samples. The diffuse reflectance is found to be always below 2%, in the mean below 1% in the spectral range of 250 nm to 900 nm. In contrast, the total hemispherical reflectance, which includes the diffuse and the specular reflectance, ranges from 5% to 45%. This shows that the slightly rough rear surface of these samples behaves optically almost like a planar surface, which justifies to assume planar surfaces in the optical model used in the fit.

The spectral reflectance of three FZ samples with different SiN_y-SiRiON stacks is exemplarily shown in Figure 4. As can be seen, the shape of the spectra already changes significantly upon a change of the layer thickness by 10 nm to 20 nm.

3.5 Determined film thicknesses

The proposed approach to fit the reflectance of thin dielectric double layers is applied to the whole set of samples and the fitted layer thicknesses are compared to the ellipsometric measurements in order to qualify the fit result. The spectral ellipsometer data of the single-film FZ samples are used as reference for all samples, represented by the solid lines in Figure 5 and Figure 6. The determined thicknesses of the layers are compared to this reference and the other ellipsometric measurements.

On the planar FZ samples (Figure 5), the fitted thicknesses of the SiN_y and the SiRiON layer agree with deviations less than 5 nm with the results of the spectral ellipsometer. It should be emphasized that no change of the fitted SiN_y thickness with increasing SiRiON thickness is observed, in contrast to the measurement results of the laser ellipsometer.

On the rough Cz samples (Figure 6) again a similar trend is observed. The fit algorithm yields the SiN_y thickness independent of the SiRiON thickness.

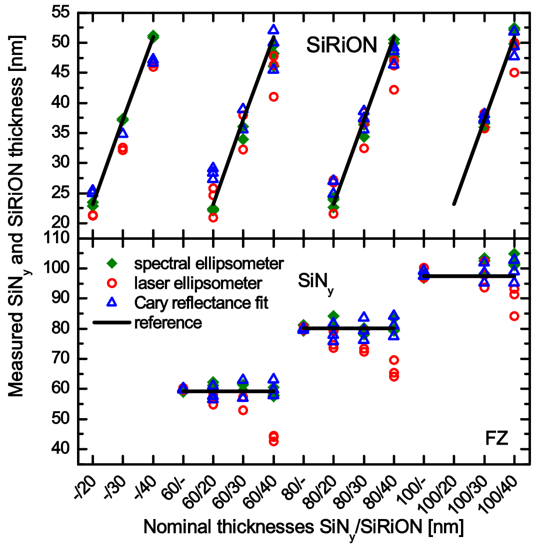

Figure 5: Comparison of the thickness results for the SiRiON layers (top) and the SiN_y layers (bottom) determined by different methods for all layer stacks manufactured on planar FZ wafers. The solid lines represent the reference layer thicknesses, i.e. the spectral ellipsometry data for single-film samples. The layer thicknesses determined from the spectral ellipsometer and from the high-precision Cary reflectance fit agree with each other and the reference, whereas the laser ellipsometer yields significantly lower thicknesses of the SiN_y layer when measured in the stack.

Moreover, the SiRiON thickness corresponds to the thickness determined by spectral ellipsometry on the planar reference samples, as shown in Figure 6 by the small deviations of the results from the black solid lines.

4 DISCUSSION

For the planar FZ samples, the results obtained with the spectral ellipsometer and with the reflectance fit match closely with each other. Therefore, we successfully validated the presented approach.

The apparent deviations of the SiN_y thickness as determined with the laser ellipsometer from the nominal film thickness (see Figure 5 and Figure 6) are regarded as artifacts. These are attributed to the fact that the laser ellipsometer can access less of the samples' physical information due to its restriction to a single wavelength, which results in a rather high uncertainty. The present measurement setup of the laser ellipsometer is therefore regarded as rather unsuitable for precise measurements on double-layer stacks. On the planar FZ samples (Figure 5), the fitted thicknesses of the SiN_y and the SiRiON layer agree with deviations less than 5 nm with the results from the spectral ellipsometer. We therefore assume that these two instruments determine the correct SiN_y layer thickness, which is assumed independent of the SiRiON thickness and rather constant for a given nominal thickness, even in the case of the Cz samples. Hence, the reflectance fit is – at least in the present case – more reliable for determining film thickness in double-layer stacks than the laser ellipsometer.

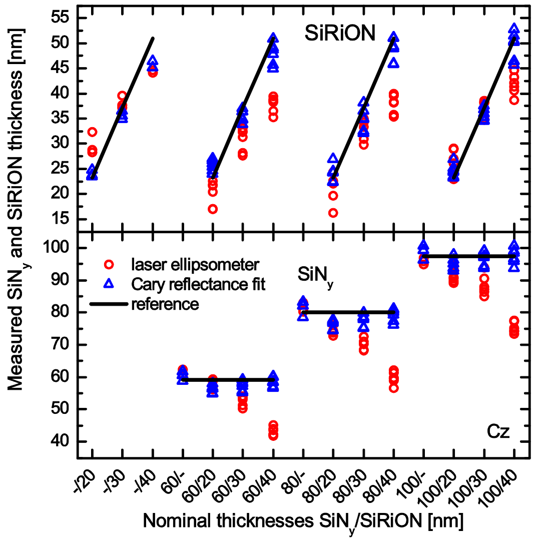

Figure 6: Comparison of the thickness results for the SiRiON layers (top) and the SiNy layers (bottom) determined by different methods for all layer stacks manufactured on wet-chemically polished Cz wafers. The solid lines represent the reference layer thicknesses, i.e. the spectral ellipsometry data for single-film FZ samples. A similar behavior as for planar float zone wafers is observed: The laser ellipsometer yields significantly smaller thicknesses of the SiN_y layer when measured in the stack with the deviation from the reference values increasing with increasing thickness of the second layer. The results of the high-precision Cary reflectance fit agree well with the reference layer thicknesses. Measurements with the spectral ellipsometer were impossible on Cz samples due to depolarization of the scattered light.

5 CONCLUSION

In order to characterize thin dielectric double-layer stacks inline allowing for a thorough process monitoring during the production of solar cells with a passivated rear surface, an approach based on a curve fit of the spectral reflectance using the transfer-matrix algorithm is presented. It is successfully validated on planar and rough silicon wafers coated with a double-layer stack of varying thickness by comparison with ellipsometric measurements, which themselves are evaluated in terms of accuracy. On the planar samples, the thicknesses determined with the curve fit agree within less than 5 nm with the results of the spectral ellipsometer. A similar trend of the fitted layer thicknesses as on the planar samples is observed on the rough samples that are typical for an industrial process sequence for the production of solar cells with passivated rear surface. Hence, the presented approach of fitting the reflectance suits the needs of characterizing the dual-layer passivation stacks at the rear surface of PERCs. Measurements with the current setup of the spectral ellipsometer are impossible on these rough samples, probably due to depolarization of the incident white light caused by the rear surface roughness. Except for the SiN_y layer thickness measured in double-layer stacks, where systematic errors of the ellipsometer of up to 20 nm are observed, the measurements with the laser ellipsometer agree well with the fit and the spectral ellipsometer, showing the robustness of the fit.

6 ACKNOWLEDGEMENTS

This work was funded by the German Federal Ministry for Economic Affairs and Energy within the framework of the project “QUASSIM-PLUS” (contract number 0325493A).

7 REFERENCES

[1] A. W. Blakers, A. Wang, A. M. Milne, J. Zhao, and M. A. Green, “22.8% efficient silicon solar cell,” *Appl. Phys. Lett*, vol. 55, no. 13, pp. 1363–1365, 1989.

[2] S. W. Glunz, R. Preu, and D. Biro, “Crystalline Silicon Solar Cells: state-of-the-art and future developments,” in *Comprehensive renewable energy*, A. Sayigh, Ed, Oxford: Elsevier, 2012, pp. 353–387.

[3] D. K. Schroder, *Semiconductor material and device characterization*, 3rd ed. Hoboken, New Jersey, USA: John Wiley & Sons, 2006.

[4] M. F. Saenger, J. Sun, M. Schädel, J. Hilfiker, M. Schubert, and J. A. Woollam, “Spectroscopic ellipsometry characterization of SiNx antireflection films on textured multicrystalline and monocrystalline silicon solar cells,” *Photovoltaics, solar energy materials and thin films - IMRC 2008, Cancun, Mexico*, vol. 518, no. 7, pp. 1830–1834, 2010.

[5] S. C. Siah, B. Hoex, and A. G. Aberle, “Accurate characterisation of silicon nitride films on rough silicon surfaces by ellipsometry,” *Proceedings of the SiliconPV 2011 Conference (1st International Conference on Crystalline Silicon Photovoltaics)*, vol. 8, no. 0, pp. 122–127, 2011.

[6] B. L. Sopori, “Principle of a new reflectometer for measuring dielectric film thickness on substrates of arbitrary surface characteristics,” *Rev. Sci. Instrum*, vol. 59, no. 5, p. 725, 1988.

[7] J. A. Dobrowolski, F. C. Ho, and A. Waldorf, “Determination of optical constants of thin film coating materials based on inverse synthesis,” *Appl. Opt*, vol. 22, no. 20, p. 3191, 1983.

[8] M. Ylilammi and T. Ranta-aho, “Optical determination of the film thicknesses in multilayer thin film structures,” *Thin Solid Films*, vol. 232, no. 1, pp. 56–62, 1993.

[9] M. Sreemany and S. Sen, “A simple spectrophotometric method for determination of the optical constants and band gap energy of multiple layer TiO2 thin films,” *Materials Chemistry and Physics*, vol. 83, no. 1, pp. 169–177, 2004.

[10] H. A. Macleod, *Thin-film optical filters*, 2nd ed. Bristol: Adam Hilger, 1986.

[11] J. Seiffe, L. Weiss, M. Hofmann, L. Gautero, and J. Rentsch, “Alternative rear surface passivation for industrial cell production,” in *23rd EUPVSEC Valencia: 2008*, 2008, pp. 1700–1703.

[12] M. A. Green, “Self-consistent optical parameters of intrinsic silicon at 300K including temperature coefficients,” *Sol. Energy Mater. Sol. Cells*, vol. 92, no. 11, pp. 1305–1310, 2008.

[13] Guido van Rossum, *Python reference manual*. Available: www.python.org.

[14] Eric Jones, Travis Oliphant, Pearu Peterson, and others, *SciPy: Open Source Scientific Tools for Python*. Available: www.scipy.org.

[15] K. Levenberg, “A method for the solution of certain problems in least squares,” *Quarterly of Applied Mathematics*, vol. 2, pp. 164–168, 1944.

[16] D. W. Marquardt, “An Algorithm for Least-Squares Estimation of Nonlinear Parameters,” *Journal of the Society for Industrial and Applied Mathematics*, vol. 11, no. 2, pp. 431–441, 1963.

[17] G. Kästner, M. Zimmer, K. Birmann, F. Souren, J. Rentsch, and R. Preu, “Single side polish etching for the rear side of crystalline silicon wafers,” in *25th EUPVSEC Valencia: 2010*, 2010, pp. 2055–2058.

[18] G. E. Jellison and F. A. Modine, “Parameterization of the optical functions of amorphous materials in the interband region,” *Appl. Phys. Lett*, vol. 69, no. 3, pp. 371–373, 1996.

[19] D. Pysch, “Assembly and analysis of alternative emitter systems for high efficient silicon solar cells,” Dissertation, Fachbereich Physik, Universität Konstanz, Germany.