University *of Ljubljana*
Faculty *of Electrical Engineering*

Tržaška 25
POB 2999
1001 Ljubljana, Slovenia
Phone:+386 1 476 84 11
Fax:+386 1 426 46 30
www.fe.uni-lj.si

Prof. Dr. Janez Krc
Faculty of Electrical Engineering
University of Ljubljana
E-mail: janez.krc@fe.uni-lj.si
Phone: +386 1 4768 843

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Evaluation report of the Doctoral Dissertation

of the candidate **Ing. Zuzana Mrázková**

entitled
Modeling and characterization of materials and nanostructures for photovoltaic applications

1. The topic of the thesis

Photovoltaics is the renewable energy technology with the largest scope for cost reduction and efficiency gains in electrical energy production. It consists of a long value chain starting from materials and structures for efficient devices, enabling reliable PV system installations. In this doctoral dissertation the candidate focused on optical modeling and characterization of materials and nanostructures for silicon photovoltaics. The emphasis is put on proper analysis and evaluation of the optical characterization results by means of modelling. In particular, the thesis focuses on optical characterization and modelling of two important light management structures: random pyramidal texture in crystalline silicon (c-Si) solar cells and innovative approach of using nanowires for radial-junction solar cells. For both approaches models have been developed and advanced characterization techniques employed for detailed analysis and optimization of structures and devices. The developed models enable the calculation of reflection and transmission properties of various pyramidal textures including thin-film stack and effective medium theory model to describe basic optical properties of silicon nanowires also during their growth. The advanced characterization techniques include reflection transmission and spectroscopic ellipsometry, particularly focused on in-situ Mueller matrix ellipsometry.

I evaluate the topic and the specific research presented in the thesis as timely and relevant.

2. The structure of the thesis

Main part of the doctoral thesis consists of 6 chapters followed by Conclusions and Perspectives. The abstract includes the main highlights of the thesis. The first chapter appropriately introduces the reader to the topic and the last one summarizes the work and gives an outlook. The Bibliography includes 87 references, among them are mainly journal papers, conference contributions, books, a patent, which are all relevant to the field in my opinion.

The structure of the thesis is appropriate. It is clear and includes all parts of a scientific thesis.

3. The contents of the thesis

Chapter I is the introduction to the thesis: The candidate highlights the importance of energy production. She explains the role of photovoltaics among the renewable energy sources. State-of-the-art solutions in relation to the pyramidal textures on c-Si wafer and Si nanowire solar cell is reviewed briefly and linked to the reference papers. The objectives of the thesis are explained, among them are deeper study and understanding of various pyramidal textures that are obtained on Si wafers and in-situ and ex-situ ellipsometry characterization of Si nanowires for radial-junction solar cells. For both modeling has been employed to give the right interpretation of the measured results.

Chapter 2 briefly describes fabrication techniques used for preparation of the samples. Among them are the PECVD and VLS processes for deposition of thin films and nanowire growth. Examples of pyramidal textures that are studied in the thesis and their etching and post treatment steps are described. Structure of hetero-junction silicon and radial-junction solar cells are introduced. As the candidate was not directly involved in the preparation of samples, but rather the advanced modelling and characterization was the topic of the thesis, the details of processes are not described in too many details, description is just on the right level for the purpose of the thesis.

In Chapter 3 the candidate describes and shows the measurement setups that she used for advanced characterization of the samples: reflection-transmission-absorption spectroscopy with an integrating sphere, standard ellipsomety setup and the Angular resolved Mueller matrix polarimetry setup. The chapter is nicely coupled with the next one where theoretical descriptions of the main measurement principles are explained.

Chapter 4 gives theoretical background for the development and use of optical models and characterization techniques. The starting point are Maxwell equations, then general equations for light propagation in non-absorbing and absorbing media. The Yen's matrix formalism is presented as it was used as a basis for optical simulation of multi-layer systems, such as thin layers in heterojunction solar cell structure. In the last part principles of ellipsometric techniques are introduced with emphasis on Mueller matrix polarimetry. Parameters I_S and I_C which are then used later in the thesis to describe optical response of materials and nanostructures are introduced here. Different dispersion models of dielectric functions of materials are briefly reviewed.

In Chapter 5 results of the research on pyramidal textures are presented. Six types of samples fabricated either by two different etching procedures (both based on KOH) or duration of the

applied post-treatment are followed in the analysis. Characterization results revealed that the actual vertex angle of the pyramids can deviate unexpectedly from the theoretical one related to <111> crystallographic planes (70.52°, forming the base angle of 54.74°). In the measured samples two different values of vertex angles obtained by different etching procedure (both using KOH) were measured to be 75° and 80° (confirmed by SEM and optical measurements). Further characterization with STEM-HAADF reveals that atomic steps on the walls are responsible for that. This affects optical performance of the texture as well as implies important consequences for the surface passivation and thin film deposition. This nanoscopic terrace-like morphology of the pyramid walls leads also to scattering of light outside the predicted angles. An efficient optical model was developed to simulate the reflection at pyramid textures. The model is based on raytracing method, assuming double reflection at flat facets. The model enabled interpretation of measured reflectance data and agrees with the experiments very well. In the second step the textures pyramids were covered with thin layers to form hetero-junction silicon solar cells. The developed model was upgraded to consider the multi-layer stack and used for the analysis of ellipsometric measurements on the samples. Moreover, the model was used to minimize optical losses in thin layers by layer thickness variations.

One of the important scientific contributions in this chapter is the explanation and understanding of the effect of different pyramid vertex angle formation and facets nano structure, explaining optical properties of the real structure. It is also an important issue that should be considered in optimization of passivation of the textured wafer in solar cells.

In Chapter 6 results of the research on optical characterization and modeling of Si nanowires are presented. In-situ Mueller matrix spectrometry is used and combined with the Bruggemann effective medium theory to model optical properties of nanowires also during the growth. The structure was sliced into more effective layers and the volumetric fraction of the material (Sn, Si) was determined based on fitting the ellipsometry data with the model. This enabled to extract the thickness and length of nanowires during the growth, as a function of the deposition time.

One of the important scientific contribution in Chapter 6 is a simple and efficient optical model for the analysis of the in-situ ellipsometry measurements and estimation of nanowire length and thickness during the nanowire growth.

4. The methodology used

The candidate covered theoretical background, selected optical characterization methods are nicely coupled with the modelling. Actually the developed models and applied approaches are very important to understand and explain the results obtained by measurements. This gives an important added value of the thesis.

5. Scientific publications

According to the list of publications and Web of Science database, the candidate is:

- 3-times co-author of articles published in peer-reviewed journals (2-times first author) and in one article in submission
- 5-times co-author of publications in conference proceedings (4-times first author)

- co-author in 14 conference contributions (7-times oral contribution)

I evaluate the quality and quantity of the candidate's bibliography as appropriate. It reflects the scientific impact of the work on the international level

6. Final assessment of the thesis

Based on overall evaluation of the thesis of the candidate Ing. Zuzana Mrázková entitled *Modeling and characterization of materials and nanostructures for photovoltaic applications* **I propose the highest evaluation grade of the thesis. The dissertation includes important scientific contributions to the field of photovoltaics and nano sciences.**

Sincerely,

Prof. Dr. Janez Krc