Report on the thesis of Aniela Czudek, titled "Impact of alkali element doping of the electrical characteristics of $Cu(In,Ga)Se_2$ solar cells and thin films"

Mrs. Czudek presents and substantiates in her thesis an alternative model on the impact of alkali doping in $Cu(In,Ga)Se_2$ chalcopyrite thin film solar cells. This is an important and timely issue, since thin film solar cells have an essential role to play in mitigating the climate crisis and since their efficiency has been boosted by the addition of alkalis, like Na or K. The fact that alkalis increase the (effective) doping of chalcopyrite films and solar cells has been known for a long time. The effect is usually explained by the influence of alkalis on doping point defects in the bulk of the chalcopyrite. An alternative model based on the passivation of grain boundary defects had been proposed in the literature, but Mrs. Czudek provides quantitative support to the model, based on measurements on thin films and on solar cells, combined with detailed simulations.
After a short introduction that motivates the topic in general, the necessary background is given on the material, the device structure, the electronic structure and in particular the effect of alkalis. This is followed by a short chapter motivating the questions and the approach of the thesis. This is unusual, but makes the motivation much more intelligible since the background has been already explained. The next two chapters give a short introduction to the methods used and to the sample series investigated, together with a description of the concrete experiments. The description of the experimental methods is very concise and presents the background and the theory of the analysis. This is followed by the two main chapters of the thesis: results and discussion. The results chapter presents the measurement results for Na and for K treatment separately, in each case divided for the relaxed state and the metastable state – this structure makes it easier for the reader to find results back. The discussion chapter brings the results previously presented together, by plotting them into suitable graphs that allow to appreciate the similarity between different measurements. These plots are particularly appreciated since they convey in a very convincing manner that the effect of Na and of K is essentially the same. One of the main parts is the discussion of the results in terms of grain boundary effects, which is partly based on the model by Baccarani et al. found in the literature and on own simulations, which support quantitatively the grain boundary model. The interpretation of the model by Baccarani appears a bit too naïve and has some flaws. The main results are untouched by this misunderstanding since the main comparison is between the experimental results and the simulation, not the analytical model by Baccarani. The conclusions drawn could have been even stronger, if the analysis had also been done for the

competing model of increased doping concentration through alkalis. The final discussion section is on the persistent photoconductivity effect, where similarities are presented, but no model to explain them. The thesis closes with conclusions and an outlook. The structure is logical and well presented.

Chapter 5 gives a very comprehensive, albeit very concise, overview of the literature concerning effects of Na and K in chalcopyrite films and discusses all the major models that appear in the literature. The same is true for the discussion of persistent photoconductivity in chapter 4. Chapter 7 briefly discusses the background of the measurement methods used in the thesis with adequate references to the literature, which introduced these methods. What is missing somewhat here is a critical debate about the limitations of these methods in thin film devices. However, this omission is justified, as it has no influence on the further analysis, which is based entirely on trends (instead of absolute values) of the extracted doping densities.

The methods used are absolute appropriate for the task at hand. Thin films and complete devices have been studied and compared, which substantiates the statement that the observed effect are bulk effects and not interface effects. The samples were obtained from an external partner but were made for the purpose of the study and allow to investigate the influence of different alkali concentrations – a study that is rarely or never done in the literature.

Understanding why alkali treatments improve the efficiency of chalcopyrite solar cells, has huge potential practical applications. This insight can help to improve solar cells even further and help industry in making better products.

The thesis provides an original solution to the scientific problem to understand the effects of alkali treatments on chalcopyrites. It is original, because it looks at series of similar samples with different alkali concentrations and because it makes strong and convincing links between Na and K treatments. It is the first time that the model of grain boundary passivation by alkalis is investigated quantitatively for a series of alkali concentrations.

The thesis clearly demonstrates Mrs. Czudek's grasp of the materials physics, electrodynamics and device physics, needed to understand and analyse these samples. Mrs. Czudek has proven that she can work as an independent scientist.

The thesis accumulates a huge amount of work and data. The data is very well structured and presented. The work comprises highly non-trivial experimental methods and their analysis plus a convincing simulation approach. I would therefore support that the thesis is distinguished, subject to a distinguished defence.

Prof. Dr. Dr. h.c. Susanne Siebentritt
TDK Europe Professor, Head of Laboratory for Photovoltaics
Department of Physics and Materials Science
physics.uni.lu/research/photovoltaics
41, rue du Brill, L-4422 Belvaux, susanne.siebentritt@uni.lu, +352-466644-6304

UNIVERSITÉ DU LUXEMBOURG