Master’s Thesis Engineering Technology

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Development of ultra-thin CIGS absorber material with alkali treatment for solar cell production

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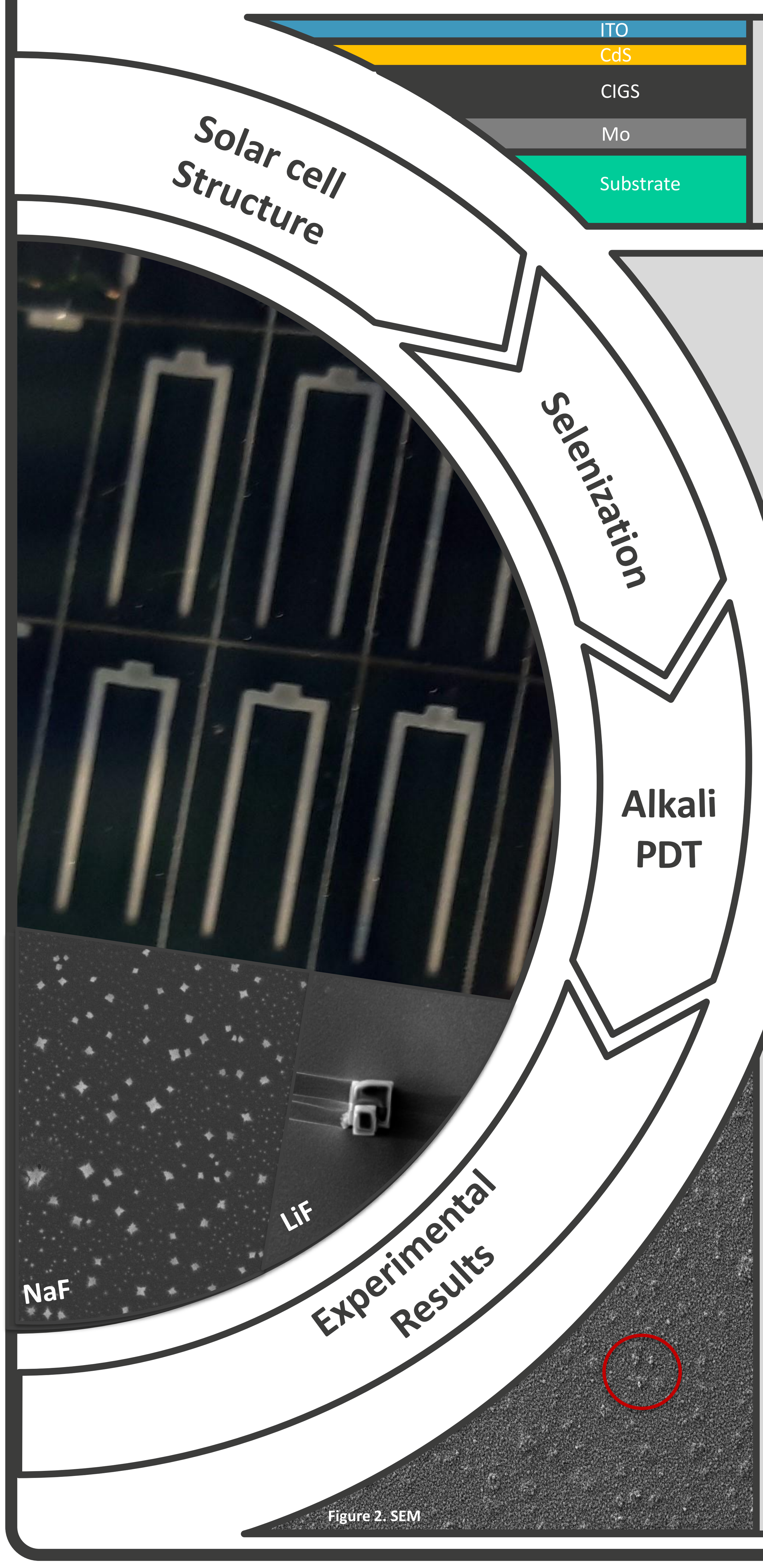
Introduction

With the depletion of natural resources and the demand for electricity increasing year by year, new and existing methods for generating renewable electricity have come to the forefront. Solar energy is considered the most effective solution because of its availability and abundance. But in order to keep solar energy viable, it will need to compete against the more conventional energy sources like coal, oil or nuclear energy. To ensure this, cost-effective reproducibility and reliable fabrication methods will need to be established in order to deliver efficient functioning solar cells.

Compared to the typical crystalline silicon solar cells, thin film technologies like $Cu(In,Ga)Se_2$ (CIGS) are a topic of interest due to their potential lighter weight, lower cost, substrate flexibility and enhancement via alkali PDT [1],[2]. With these topics in mind, the goal of this work is to create a baseline for the selenization of CIGS absorber layers and improve the electrical and optical characteristics of these absorbers with the incorporation of alkali elements via post-deposition treatments (PDT).



General Solar cell structure:

- Intrinsic Zinc Oxide (ITO) layer
- Cadmiumsulfide (CdS) layer
- Absorber (CIGS) layer
- Soda-lime glass (SLG) substrate with Molybdenum (Mo) layer

Selenization sample specifics:

- SLG = 3.1mm thick
- CIGS formed by Annealsys-One tool
- Extra coat of Si(O,N) between Mo and CIGS for preventing alkali diffusion from SLG
- Sample size 2,5x5cm

Alkali sample specifics:

- SLG = 1mm thick
- CIGS formed by Co-evaporation
- No extra coat of Si(O,N) against alkali diffusion
- Sample size 2,5x5cm

Baseline Selenization recipe (Figure 1):

- Selenization Temperature 510/530/550°C
- Annealing time 15 min
- 20 sccm H_2Se flow

Addition of N_2-step (blue):

- Pre-annealing to homogenize metallic precursor
- For 7 min at 350°C

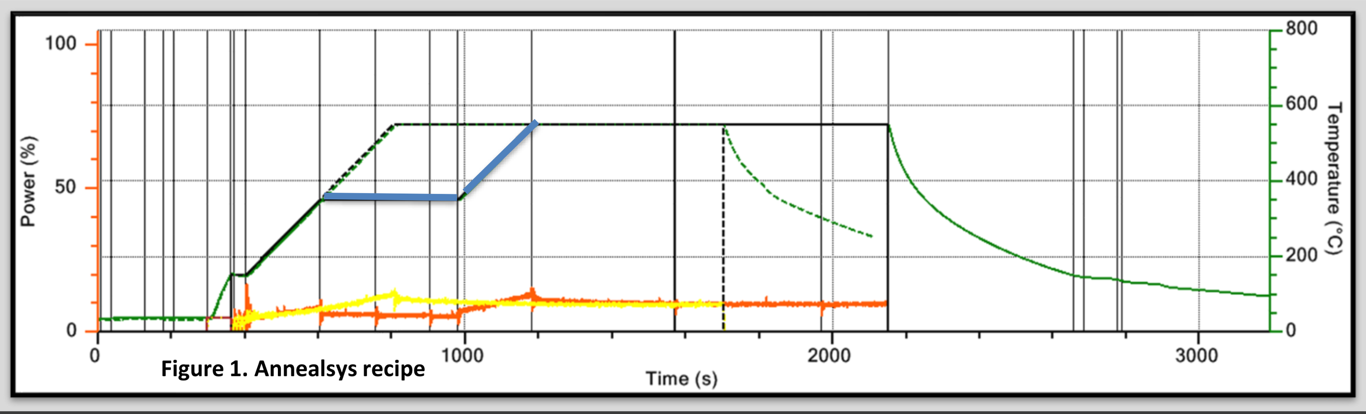


Figure 1. Annealsys recipe

Co-Evaporated CIGS Sample

Sample Cleaning:

- 5 min in NH_4OH (10%)
- 5 min in H_2O
- Dry blowing with N2-gun

Preparing Solution:

- 0,2M alkali salt
- LiF/NaF/KF/RbF/CsF
- LiCl/NaCl/KCl

Spin Coater:

- Fixed speed/acc.
- To create homogeneous layer

PEO-Furnace:

- Promote alkali diffusion
- At 350°C in N_2-atmosphere
- For 30 min

Characterization:

- SEM
- PL
- IV-measurements

Figure 2. SEM

Selenization:

- Higher selenization temperature:
  → More observed In islands (Figure 2)
  → Better IV characteristics (Figure 3)
- Added N_2 pre-annealing step
  → Improved CIGS surface morphology

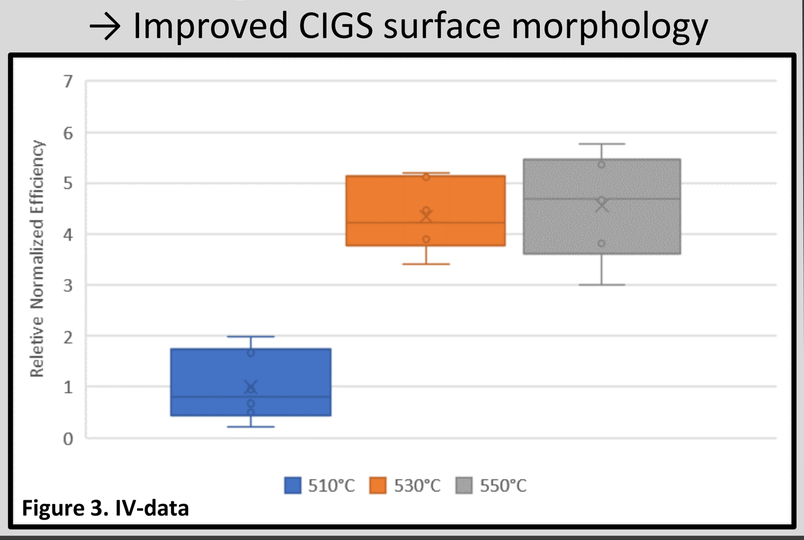


Figure 3. IV-data

Alkali PDT:

- Improved the quality of the CIGS bulk → due to increased PL peak intensities (Figure 4)
- No significant difference between XF and XCl PDT
- Poor IV performance → due to possible oxide layer between CdS and i-ZnO
- Obtained alkali crystals on top of CIGS absorber layer (NaF/LiF) → interesting for developing front passivation

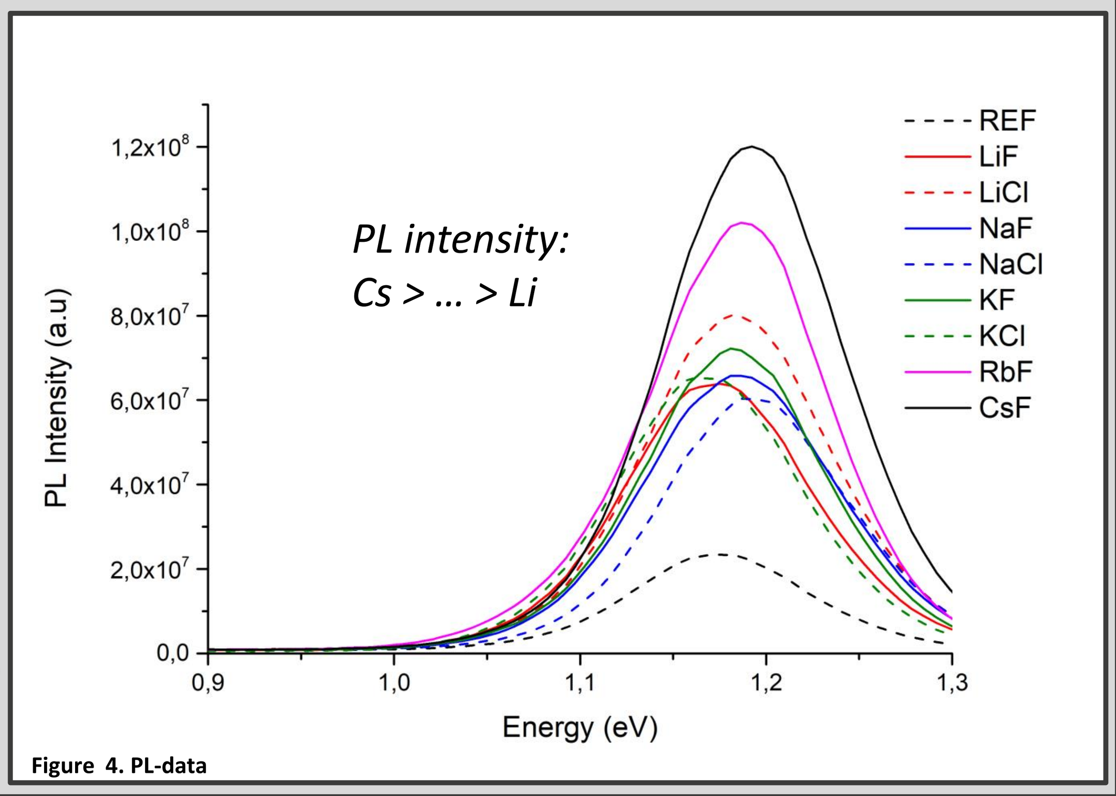


Figure 4. PL-data

Conclusion

For the selenization part, IV-data showed an increase in solar cell characteristics with higher anneal temperatures. This favored reaction kinetics of CIGS over CIS, meaning that at a higher temperature more CIGS phase was formed, and a better intermixing took place between CIS and CGS. This then resulted in more Ga at the front of the absorber layer, explaining improved solar cell performance. SEM images from the N_2 pre-annealing experiment runs showed a decrease in the In islands in combination with a smoother CIGS surface, presumable due to a better intermixing between the four elements. However, IV data suggested that with the addition of this step, significant shunt paths had developed due to the formation of In bulbs, resulting in very poor IV performance.

The alkali PDT resulted in creating an improved quality of CIGS bulk, with higher PL intensities measured for the sample treated with larger alkali atom size. This means that for all the fluorides, CsF showed the highest PL intensity, suggesting that Cs reduced non-radiative recombination possibilities due to filling up defects in the CIGS absorber layer. Further into the developing process it was discovered that an unwanted oxide layer may be present between the CdS and i-ZnO layer. This process of oxidation presumably started in the preparation phase of the i-ZnO deposition and got stimulated by the fact that there were alkali atoms present in the CIGS absorber layer. Resulting in poor IV performance for the treated solar cells.

Supervisors / Co-supervisors / Advisors

Prof. Dr. Vermang Bart
Kohl Thierry

[1] F. Kessler and D. Rudmann, “Technological aspects of flexible CIGS solar cells and modules,” Sol. Energy, vol. 77, no. 6, pp. 685–695, 2004

[2] P. Jackson, R. Wuerz, D. Hariskos, E. Lotter, W. Witte, and M. Powalla, “Effects of heavy alkali elements in Cu(In,Ga)Se2 solar cells with efficiencies up to 22.6%,” Phys. Status Solidi - Rapid Res. Lett., vol. 10, no. 8, pp. 583–586, 2016

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