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**IMPACT OF SULFUR ANNEALING ON THE  
 $\text{Cu}_2\text{ZnSnS}_4$  MONOGRAIN POWDER PROPERTIES  
AND SOLAR CELL PARAMETERS**

**VÄÄVLI AURURÕHU TÖÖTLUSTE MÕJU  $\text{Cu}_2\text{ZnSnS}_4$   
MONOTERAPULBRITE OMADUSTELE JA  
PÄIKESEPATAREI VÄLJUNDPARAMEETRITELE**

MASTER THESIS

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## **Impact of sulfur annealing on the $\text{Cu}_2\text{ZnSnS}_4$ monograin powder properties and solar cell parameters**

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Kesterite materials like  $\text{Cu}_2\text{ZnSnS}_4$  have drawn considerable attention due to the necessity to replace expensive and rare Indium and Gallium in Copper Indium Gallium Selenide (CIGS) solar cells with more abundant materials like Zinc and Tin. These materials are not commercially available yet. Currently, the efficiency of  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) monograin layer solar cells is mainly limited by the recombination losses in the bulk and at the surface of absorber/buffer that need to be reduced. One approach to significantly improve the performance of CZTS monograin layer solar cells is to post-treat the monograin powder crystals` before the buffer layer deposition.

The objective of this research was to study the impact of post-treatment regime (annealing of as-grown powder crystals at high temperatures in a sulfur-containing atmosphere before the deposition of CdS) on the surface and bulk composition of CZTS MGP crystals and MGL solar cell parameters. In this work, the high-quality  $\text{Cu}_2\text{ZnSnS}_4$  monograin powder absorber materials were synthesized in vacuumed quartz ampoules from high purity (5N) binary precursors CuS, SnS and ZnS in the liquid phase of KI (4N) by molten salt method. The chemically etched monograin powders were annealed at different temperatures (550, 650, 750 and 850 °C) under different sulfur vapor pressures (100, 1000, 2050 Torr) in a two-zone furnace in closed ampoules. In addition a series of experiments were performed by adding inert argon gas to the sulfur atmosphere. Four different pressures of argon were used (10, 50, 100, and 300 Torr). MGL solar cells were prepared from the different powders having a superstrate structure of graphite(gold)/CZTS/CdS/i-ZnO/ZnO:Al/Ag/glass.

Chemical composition of monograins was analyzed by EDX and Raman spectroscopy. ZnS and  $\text{SnS}_2$  secondary phases were found on crystals` surfaces after all the post-annealing processes. At the same time, Cu content in the bulk of post-annealed crystals increased and Zn content decreased. By EBIC, it was seen that the presence of  $\text{SnS}_2$  on the surface of monograins had a negative effect on MGL solar cells performance. However, *I-V* characteristics of MGL solar cells showed remarkable improvement after post-annealing in sulfur atmosphere compared to the parameters of solar cell based on un-annealed absorber material. Subsequent experiments with the addition of argon to the sulfur atmosphere were carried out and they had detrimental effect for solar cell parameters. The best efficiency of 8.42% was obtained with the solar cell based on CZTS monograin powder annealed at 850 °C in a 2050 Torr sulfur atmosphere.