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Dr.-Ing. Björn Jakob Müller,
Frankfurt am Main

# Improvement of $Cu(In,Ga)(S,Se)_2$ thin film Solar Cells with the help of Gallium and Sulfur Gradients

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# Improvement of $Cu(In,Ga)(S,Se)_2$ thin film Solar Cells with the help of Gallium and Sulfur Gradients

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Das Ziel der Arbeit besteht darin, optimierte Absorber für das Dünnschicht Solarzellensystem Cu(In,Ga)(S,Se)$_2$ mit Hilfe von industrienahen Prozessen herzustellen. Der industrienahe zweistufige Herstellungsprozess beinhaltet das Aufbringen von metallischen Vorläuferschichten (Kathoden zerstäubung & thermische Verdampfung) und die Bildung des Chalkopyrit Absorbers in Folge des thermischen Ausheizschrittes. Der gezielte Einbau von Konzentrationsgradienten bestehend aus Ga/In und Se/S wird werkstoffseitig am Absorber strukturell analysiert und für die elektronischen Eigenschaften der Solarzelle optimiert. Zur Justage des Ga/In Profils werden sowohl das optimierte Temperaturprofil als auch ein Überangebot an Chalkogenen verwendet. Für die Einstellung des Se/S Profils im Chalkopyrit dienen das Ausgangsverhältnis sowie ein nachträglicher S Einbau (Erweiterung auf einen drei-stufigen Prozess). Um den Rückkontakt der Solarzelle vor den aggressiven Chalkogenen während des Prozesses zu schützen, wurde eine Mo-N Diffusionsbarriere entwickelt.

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# Inscription

To my parents
and to my brother.

# Contents

# Nomenclature

The following abbreviations, symbols and codes are used in the thesis:

**a:** Lattice constant

$a(E)$**:** Absorptance

**Ag:** Silver

**Al:** Aluminium

$\alpha$**:** Absorption coefficient

$\alpha_{eff}$**:** Effective absorption coefficient

**AZO:** Al:ZnO

**BSF:** Back surface field

$\beta$**:** Linear $E_g$ grading degree

**c:** Concentration

$c_L$**:** Speed of light

**CB:** Conduction band

**CBD:** Chemical bath deposition

**CE:** Co-evaporation

**CGI:** Cu/(Ga+In) concentration ratio

**$CuGaS_2$:** Copper Gallium Disulfide

**$CuGaSe_2$:** Copper Gallium Diselenide

$\chi$**:** Electron affinity

**$Cu(In,Ga)Se_2$:** Copper Indium Gallium Diselenide

**$Cu(In,Ga)(S,Se)_2$:** Copper Indium Gallium Disulfo Selenide

**$CuInS_2$:** Copper Indium Disulfide

**$CuInSe_2$:** Copper Indium Diselenide

**Cu:** Copper

$d_1$**:** Back grading distance

$d_2$**:** Front grading distance

$D$: Diffusion coefficient of a diluted system

$d_c$: Critical distance

**DC:** Direct current

**Di:** Diode

$d_{hkl}$: Lattice spacing distance

$D_n$: Carrier diffusion coefficient

**DOS:** Density of states

$\xi$: Electric field

$\xi_{grad}$: Electric field in graded absorber

$\mathbf{e}^-$: Electron

**EDX:** Energy dispersive X-ray spectroscopy

$E_F$: Fermi energy

$E_g$: Band gap

$E_n$: One electron energy

**EMPA:** Swiss Federal Laboratories for Materials Science and Technology

**EQE:** External quantum efficiency

$\eta$: Efficiency

**Fe:** Iron

**FF:** Fill factor

**FWHM:** Full width at half maximum

**g:** Carrier generation rate

**G:** Generation current

**Ga:** Gallium

**GDOES:** Glow discharge optical emission spectrometry

**GIXRD:** Grazing incidence X-ray diffraction

**GGI:** Ga/(Ga+In) concentration ratio

$G_h$: Hole generation current

$G_n$: Electron generation current

$\mathbf{h}^+$: Hole

$\hat{H}^{1e}_{eff}$: Effective one electron Hamiltonian

**HTG:** High temperature glass

$h\nu$: Photon energy

$\hbar\Omega$: Phonon energy

**I:** Intensity

**IF:** Interface recombination

$I_{mp}$: Current at maximum power point

**In:** Indium

**IQE:** Internal quantum efficiency

**I-V:** Current-voltage

**IXRD:** In-situ X-ray diffraction

**i-ZnO:** Intrinsic ZnO

**J:** Current density

$J_0$**:** Reverse saturation current density

$J_{bb}$**:** Photo current density, produced by black body radiation

**JCPDS:** Joint Committee on Powder Diffraction Standards

$J_{dark}$**:** Dark current density

$J_{atom}$**:** Material flux

$J_{ph}$**:** Photo current density, occurs according to absorbed photons

$J_{rec}$**:** Recombination current density

$J_{sc}$**:** Short-circuit current density

$J_{sc}^{grad}$**:** Short-circuit current density calculated by analytical approach

$J_{sc}^{SCAPS}$**:** Short-circuit current density calculated by SCAPS simulations

$J_{tot}$**:** Total current density

**K:** Pottasium

$k_B$**:** Boltzmann constant

$k_e$**:** Extinction coefficient

$\vec{k}$**:** Scattering vector

$L_\alpha$**:** Absorption length

$L_n$**:** Electron diffusion length

$L_p$**:** Hole diffusion length

$M$**:** Diffusion coefficient

**mc-Si:** Multicrystalline silicon

**MoN:** Molybdenum nitride

**$MoS_2$:** Molybdenum disulfide

**$MoSe_2$:** Molybdenum diselenide

**$MoSSe_2$:** Molybdenum disulfoselenide

$\overline{n}$**:** Complex refractive index

$n_r$**:** Refractive index

**Na:** Sodium

$N_A$**:** Acceptor density

$\nabla$**:** Gradient

$N_C$**:** DOS in the CB

$N_D$**:** Donor density

$n_{id}$**:** Diode ideality factor

**NREL:** National Renewable Energy Laboratory

$N_V$: DOS in the VB

**n-ZnO:** n-doped ZnO

$\Delta n$: Excess charge carrier density (electrons)

**ODC:** Ordered defect compound

**PL:** Photoluminescence

$P_{mp}$: Maximum electrical power

$P_{opt}$: Power of incoming photons

$\Psi$: Electrostatic potential

**p-Si:** Polycrystalline silicon

**PV:** Photovoltaics

$\phi_{sun}$: Photon flux from the sun

$\phi(V,E)$: Emitted photon flux, depending on voltage and energy

$\Delta p$: Excess charge carrier density (holes)

**Q:** Material quantity

**QNR:** Quasi neutral region

**R:** Recombination current

$\rho$: Charge distribution

$R_h$: Hole recombination rate

$R_n$: Electron recombination rate

$R_p$: Parallel resistance

$R_s$: Series resistance

**RTP:** Rapid thermal processing

**S/metal:** S/(Cu+Ga+In) concentration ratio

**S:** Sulfur

**SCAPS:** Solar Cell Capacitance Simulator

**SCR:** Space charge region

**Se/metal:** Se/(Cu+Ga+In) concentration ratio

**Se:** Selenium

**SEL:** Stacked elemental layer

**SEM:** Scanning electron microscopy

**SFG:** Standard float glass

**SIMS:** Secondary ion mass spectroscopy

**SQ:** Shockley-Queisser

**SRH:** Shockley-Read-Hall

**SSSe:** S/(S+Se) concentration ratio

$T$: Temperature

**Te:** Tellurium

$T_S$: Sulfurization temperature

$T_{Se}$: Selenization temperature

$\mu_n$: Electron mobility

$\mu_p$: Hole mobility

**VB:** Valence band

$V_D$: Built-in potential

$v_e$: Recombination velocity for electrons

$V_{eff}$: Effective potential

$v_h$: Recombination velocity for holes

$V_{mp}$: Voltage at maximum power point

$V_{oc}$: Open-circuit voltage

$\phi_n$: One electron wave function

$W_p$: Watt peak

**XRD:** X-ray diffraction

**XRF:** X-ray fluorescence

**Zn:** Zinc

**ZnS:** Zinc blende

**ZSW:** Centre for Solar Energy and Hydrogen Research Baden-Wuerttemberg

# Abstract

The aim of this work is to optimize the absorber for $Cu(In,Ga)(S,Se)_2$ thin film photovoltaic cells in order to get a higher efficiency of the energy conversion in the framework of a well-established industrial process. In general the industrial process belongs to the family of two-step processes which consist of sputtering and evaporating a stack of elemental layers and subsequent annealing in order to form the chalcopyrite structure of the absorber. The two-step process stays in competition with the more flexible co-evaporation process, which up to now has delivered the best laboratory cells reaching efficiencies up to 22.6%. The motivation for the two-step process may also be derived from the achievement of the best module conversion efficiencies of almost 18%. The Shockley-Queisser limit of single junction solar cells is around 33%. The difference of 11% to the best laboratory cells can be explained by optical reflection and internal recombination losses (Auger and Shockley-Read-Hall) and is mostly reflected in open-circuit voltage losses. In order to achieve higher open-circuit voltages, conduction band V-profiles are introduced in order to reduce space-charge region and interface (buffer) recombination as well as back contact recombination. Band gap grading is most easily achieved in the co-evaporation process. Due to the fact that the stacked elemental layer process is driven by interdiffusion of elements and compounds the precise control of these V-profiles is a challenge and alternative ways to control the band gap profile need to be found. To adapt the electronic band structure to the back electrode and the transparent window via a buffer layer, a certain gradient of Ga and S in the absorber is needed. In this work,

optimized temperature profiles, optimal chalcogen amounts and a modified back contact have been identified as possible parameters for improvement of solar cell performance. In the field of band gap grading in Cu(In,Ga)$Se_2$ thin films a method was found to control the Ga/(Ga+In) profiles by the process temperature and the Se amount. This allows to optimize band gap profiles in the p-n junction solar cell with respect to more efficient charge carrier collection. With the help of numerical SCAPS simulations the optimized parameters of back and front surface grading properties can be calculated for the application in optimal process conditions. For the adjustment of S/(S+Se) profiles in Cu(In,Ga)$(S,Se)_2$ thin films, defined concentration gradients were established by applying chalcogens with a specific ratio before the annealing process. The conventional two-step process was furthermore modified by separating the annealing step into a pure selenization and a sulfurization phase in order to better adjust the S/(S+Se) profile. A large parameter field makes a detailed study of post sulfur diffusion processes possible. However, to adjust the chalcogen profile in the thin film it was found that the most important parameters are the sulfurization temperature and the sulfurization time in step two. Furthermore, a Mo-N layer was introduced as a novel barrier layer against chalcogen diffusion to the Mo back contact. A self-limited $MoSe_2$ layer growth on top of the Mo-N barrier layer with a defined thickness has been found, which does not hinder charge carrier collection at the back contact and additionally ensures a quasi-ohmic contact.