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

Nr. 396

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

α**:** Absorption coefficient

α_{eff}**:** Effective absorption coefficient

AZO: Al:ZnO

BSF: Back surface field

β**:** 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

χ**:** 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

ξ: Electric field

ξ_{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

η: 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_α**:** 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

∇**:** 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

Δn: Excess charge carrier density (electrons)

ODC: Ordered defect compound

PL: Photoluminescence

P_{mp}: Maximum electrical power

P_{opt}: Power of incoming photons

Ψ: Electrostatic potential

p-Si: Polycrystalline silicon

PV: Photovoltaics

ϕ_{sun}: Photon flux from the sun

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

Δp: Excess charge carrier density (holes)

Q: Material quantity

QNR: Quasi neutral region

R: Recombination current

ρ: 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

μ_n: Electron mobility

μ_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

ϕ_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.