

Reihe 9

Elektronik/Mikro-
und Nanotechnik

Nr. 396

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Frankfurt am Main

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

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Müller, Björn Jakob

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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 industrienaher zweistufiger 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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**To my parents
and to my brother.**

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Nomenclature

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

a:	Lattice constant	CGI:	Cu/(Ga+In) concentration ratio
$a(E)$:	Absorptance	CuGaS₂:	Copper Gallium Disulfide
Ag:	Silver	CuGaSe₂:	Copper Gallium Diselenide
Al:	Aluminium	χ :	Electron affinity
α :	Absorption coefficient	Cu(In,Ga)Se₂:	Copper Indium Gallium Diselenide
α_{eff} :	Effective absorption coefficient	Cu(In,Ga)(S,Se)₂:	Copper Indium Gallium Disulfide Selenide
AZO:	Al:ZnO	CuInS₂:	Copper Indium Disulfide
BSF:	Back surface field	CuInSe₂:	Copper Indium Diselenide
β :	Linear E_g grading degree	Cu:	Copper
c:	Concentration	d_1 :	Back grading distance
c_L :	Speed of light	d_2 :	Front grading distance
CB:	Conduction band		
CBD:	Chemical bath deposition		
CE:	Co-evaporation		

D:	Diffusion coefficient of a diluted system	FWHM:	Full width at half maximum
d_c :	Critical distance	g:	Carrier generation rate
DC:	Direct current	G:	Generation current
Di:	Diode	Ga:	Gallium
d_{hkl} :	Lattice spacing distance	GDOES:	Glow discharge optical emission spectrometry
D_n :	Carrier diffusion coefficient	GIXRD:	Grazing incidence X-ray diffraction
DOS:	Density of states	GGI:	Ga/(Ga+In) concentration ratio
ξ :	Electric field	G_h :	Hole generation current
ξ_{grad} :	Electric field in graded absorber	G_n :	Electron generation current
e^- :	Electron	h^+ :	Hole
EDX:	Energy dispersive X-ray spectroscopy	\hat{H}_{eff}^{1e} :	Effective one electron Hamiltonian
E_F :	Fermi energy	HTG:	High temperature glass
E_g :	Band gap	$h\nu$:	Photon energy
E_n :	One electron energy	$\hbar\Omega$:	Phonon energy
EMPA:	Swiss Federal Laboratories for Materials Science and Technology	I:	Intensity
EQE:	External quantum efficiency	IF:	Interface recombination
η :	Efficiency	I_{mp} :	Current at maximum power point
Fe:	Iron	In:	Indium
FF:	Fill factor	IQE:	Internal quantum efficiency

I-V:	Current-voltage	J_{tot} :	Total current density
IXRD:	In-situ X-ray diffraction	K:	Pottasium
i-ZnO:	Intrinsic ZnO	k_B :	Boltzmann constant
J:	Current density	k_e :	Extinction coefficient
J_0 :	Reverse saturation current density	\vec{K} :	Scattering vector
J_{bb} :	Photo current density, produced by black body radiation	L_α :	Absorption length
		L_n :	Electron diffusion length
		L_p :	Hole diffusion length
		M :	Diffusion coefficient
JCPDS:	Joint Committee on Powder Diffraction Standards	mc-Si:	Multicrystalline silicon
J_{dark} :	Dark current density	MoN:	Molybdenum nitride
J_{atom} :	Material flux	MoS₂:	Molybdenum disulfide
J_{ph} :	Photo current density, occurs according to absorbed photons	MoSe₂:	Molybdenum diselenide
		MoSSe₂:	Molybdenum disulfoselenide
		\bar{n} :	Complex refractive index
J_{rec} :	Recombination current density	n_r :	Refractive index
		Na:	Sodium
J_{sc} :	Short-circuit current density	N_A :	Acceptor density
		∇ :	Gradient
J_{sc}^{grad} :	Short-circuit current density calculated by analytical approach	N_C :	DOS in the CB
		N_D :	Donor density
J_{sc}^{SCAPS} :	Short-circuit current density calculated by SCAPS simulations	n_{id} :	Diode ideality factor
		NREL:	National Renewable Energy Laboratory

N_V :	DOS in the VB	R_p :	Parallel resistance
n-ZnO :	n-doped ZnO	R_s :	Series resistance
Δn :	Excess charge carrier density (electrons)	RTP :	Rapid thermal processing
ODC :	Ordered defect compound	S/metal :	S/(Cu+Ga+In) concentration ratio
PL :	Photoluminescence	S :	Sulfur
P_{mp} :	Maximum electrical power	SCAPS :	Solar Cell Capacitance Simulator
P_{opt} :	Power of incoming photons	SCR :	Space charge region
Ψ :	Electrostatic potential	Se/metal :	Se/(Cu+Ga+In) concentration ratio
p-Si :	Polycrystalline silicon	Se :	Selenium
PV :	Photovoltaics	SEL :	Stacked elemental layer
ϕ_{sun} :	Photon flux from the sun	SEM :	Scanning electron microscopy
$\phi(V,E)$:	Emitted photon flux, depending on voltage and energy	SFG :	Standard float glass
Δp :	Excess charge carrier density (holes)	SIMS :	Secondary ion mass spectroscopy
Q :	Material quantity	SQ :	Shockley-Queisser
QNR :	Quasi neutral region	SRH :	Shockley-Read-Hall
R :	Recombination current	SSSe :	S/(S+Se) concentration ratio
ρ :	Charge distribution	T :	Temperature
R_h :	Hole recombination rate	Te :	Tellurium
R_n :	Electron recombination rate	T_S :	Sulfurization temperature

T_{Se} :	Selenization temperature	V_{oc} :	Open-circuit voltage
μ_n :	Electron mobility	ϕ_n :	One electron wave function
μ_p :	Hole mobility	W_p :	Watt peak
VB:	Valence band	XRD:	X-ray diffraction
V_D :	Built-in potential	XRF:	X-ray fluorescence
v_e :	Recombination velocity for electrons	Zn:	Zinc
V_{eff} :	Effective potential	ZnS:	Zinc blende
v_h :	Recombination velocity for holes	ZSW:	Centre for Solar Energy and Hydrogen Research Baden-Wuerttemberg
V_{mp} :	Voltage at maximum power point		

Abstract

The aim of this work is to optimize the absorber for $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ 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 $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin films a method was found to control the $\text{Ga}/(\text{Ga}+\text{In})$ 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 $\text{S}/(\text{S}+\text{Se})$ profiles in $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ 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 $\text{S}/(\text{S}+\text{Se})$ 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.