Appendix I

Standard parameters used in this work for the growth of $CuGaSe_2$ (CGSe) absorber films in the open-tube CVD reactor, schematically shown in Figure 23 and described in Section 3.1, are summarised in Table 8.

Every CVD process includes an initial and final conditioning stage consisting in the evacuation and ventilation of the reactor in three cycles under H_2 and N_2, in order to purge the system of water vapour after mounting the substrates and source boats prior to the deposition, and to remove rests of hazardous H_2Se gas from the reactor after completing the deposition process. The reactor gas outlet is directly connected to the scrubber system, where hazardous species are neutralised with chemical solutions. The conditioning stage takes 45 minutes, and proceeds during the system heating (initial) or cooling (final conditioning).

Single-stage grown absorbers are processed with the first stage indicated in Table 8. The iodine source temperature is used to control the final [Ga]/[Cu](s) ratio. Two-stage grown absorbers are fully processed with first and second stages given in Table 8, with an intermediate substrate heating step under H_2 of 15 minutes to improve the Ga-enrichment stage. A final 5 minutes annealing under H_2 is carried out at the same substrate temperature after completion of the second stage.

Table 8. Standard parameters used for the growth of CGSe absorber films in single stage (first stage) and two-stage processes used in this work.

Parameter and units	First stage	Second stage
Deposition time (min)	240	20
Reactor pressure (mbar)	100	100
Source temperature (°C)	600	600
Substrate temperature (°C)	500	530
Iodine source temperature (°C)	40-70	-
Q_1 (ml/min)	200	0
Q_2 (ml/min)	260	460
Q_3 (ml/min)	1100	1100
Q_4 (ml/min)	300	300
Q_{HCl} (ml/min)	160	160

Appendix II

Material parameters (see Ref. [66] and references therein) used for the numerical simulations included in Chapter 4 with the software package SCAPS [200] are given in Table 9.

Table 9. Material parameters, after [66] and references therein, except where indicated: [(*)] this work; [(+)] Ref.[168]

Parameter	$MoSe_2$	$CuGaSe_2$	CdS	i:ZnO	Ga:ZnO
E_g (eV)	1.1 [(+)]	1.65 [(*)]	2.4	3.3	3.3
χ (eV)	4.2 [(+)]	4.0	4.1	4.3	4.4
N_A (cm^{-3})	10^{17} [(+)]	$2.5 \cdot 10^{16}$ [(*)]	-	-	-
N_D (cm^{-3})	-	-	$5 \cdot 10^{16}$	$5 \cdot 10^{16}$	10^{20}

List of symbols

Abbreviations

AFM	Atomic force microscopy
AM1.5G	Air Mass 1.5 Global
CBD	Chemical bath deposition
CCSVT	Chemical close-spaced vapour transport
CGSe	Copper gallium diselenide ($CuGaSe_2$)
CP	Contact potential
CVD	Chemical vapour deposition
EBIC	Electron-beam-induced current
EDX	Energy-dispersive X-ray spectroscopy
ELO	Epitaxial lift-off
EQE	External quantum efficiency
I-V	Current-voltage characteristic
I(V,T)	Current-voltage characteristic as a function of temperature
IQE	Internal quantum efficiency
KPFM	Kelvin probe force microscopy
MBE	Molecular beam epitaxy
MOCVD	Metal-organic chemical vapour deposition
OVC	Ordered vacancy compound
PV	Photovoltaics
PVD	Physical vapour deposition
QE	Quantum efficiency
QNR	Quasi-neutral region
RTP	Rapid thermal processing
SCR	Space-charge region
SEM	Scanning electron microscopy
SIMS	Secondary-ion-mass spectroscopy
SLG	Soda-lime glass
SPV	Surface photovoltage
STM	Scanning tunnelling microscopy
TCO	Transparent conductive oxide
TEM	Transmission electron microscopy
UHV	Ultra-high vacuum
UPS	Ultraviolet photoemission spectroscopy
XPS	X-ray photoemission spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

Symbols

a, a	Lattice constant
A	Diode ideality factor
α	Absorption coefficient
c, c	Lattice constant
C	Capacitance
CB	Conduction band
C_i	Mass fraction of element i
d, d_b	Buffer layer thickness
d	Lattice plane spacing
$D_{n,p}$	Diffusivity of free electrons, holes
Δ_{SO}	Spin-orbit splitting
Δ_{CF}	Crystal-field splitting
$\Delta E_{C,V}$	Conduction, valence band off-set
E, E(x)	Electric field

E	Energy level
E_A	Activation energy
E_b	Binding energy
E_C	Conduction band minimum
E_f	Energy of the final electronic state
E_F	Fermi level
E_g	Energy band gap
E_i	Energy of the initial electronic state
E_j	Magnitude of the electric field at the p-n junction
E_{kin}	Kinetic energy
E_{max}	Maximum electric field
E_{00}	Characteristic energy of tunnelling-enhanced recombination
E_T	Energy of defect level
E_V	Valence band maximum
ε	Relative dielectric constant
F_{es}	Magnitude of the electrostatic force
$F(x)$	Minority carrier collection probability
FF	Fill factor
Φ	Work function
Φ_{ph}	Photon flux
$g(E,x)$	Minority carrier generation function
Γ	Correction factor for tunnelling-enhanced recombination
η	Energy conversion efficiency
I	Current
I	Intensity
I_b	Electron beam current
I_c	EBIC current
I_{il}	Illumination intensity
J	Current density
J_{bias}	Current density under voltage bias
J_D	Diode current density
J_{diff}	Diffusion current density
J_L	Light-generated current density
$J_{n,p\,g}$	Generation current density of electrons, holes
$J_{n,p\,r}$	Recombination current density of electrons, holes
J_{mmp}	Current density at the maximum power point
J_0	Saturation current density
J_{00}	Pre-factor of the saturation current density
J_{ph}	Photocurrent density
J_R	Recombination current density
J_{SC}	Short-circuit current density
$\mathbf{k}$, k	Propagation vector
L	Minority carrier diffusion length
L_D	Debye screening length
L_{eff}	Effective minority carrier diffusion length
$L_{n,p}$	Electron, hole diffusion length
λ	Wavelength
m^*	Effective mass
μ	Minority carrier mobility
n	Free electron concentration
N	Net doping concentration
N_A	Net doping concentration in the absorber
N_b	Net doping concentration in the buffer
N_A^-	Ionised acceptor density
N_C	Conduction band effective density of states
N_D^+	Ionised donor density
N_{eff}^{abs}	Effective doping concentration in the absorber
n_i	Intrinsic free carrier concentration
$N_T(E)$	Defect density distribution
N_V	Valence band effective density of states
υ	Frequency

p, p	Momentum
p	Free hole concentration
p	Power
p	Pressure
$Q_{1,4,HCl}$	Mass flows through lines 1, 4 and HCl of the open-tube CVD reactor
Q_i	Charge density at interface states
Q_n	Charge density in the n-type window layer
r	Position
R_{A-B}	Characteristic bond length between atoms A and B
R	Recombination rate
R_{max}	Maximum recombination rate
R_g	Radius of generation volume
$R(\lambda)$	Reflectance
R_s	Series resistance
R_{sh}	Shunt resistance
ρ	Density
$\rho(x)$	Fixed charge density
S	Interface recombination velocity
σ	Charge carrier capture cross-section of electronic defect
$\Sigma(E_b)$	Minority carrier collection efficiency
t	Time
T	Temperature
T^*	Characteristic temperature of tunnelling process
T_{Iodine}	Iodine source temperature
$T(\lambda)$	Transmittance
T_{sample}	Sample processing temperature
T_{sub}	Substrate processing temperature
τ	Minority carrier lifetime
θ	X-ray diffraction angle
u	Anion displacement
U	Width of UPS spectrum
U_{ac}	ac-bias
U_{dc}	dc-bias
V(x)	Electrostatic potential
V	Potential drop, voltage
V_{app}	Applied voltage bias
VB	Valence band
V_{bi}	Built-in potential
v_{dr}	Drift velocity of charge carriers
V_{mmp}	Voltage at maximum power point
V_{OC}	Open-circuit voltage
v_{th}	Thermal velocity of charge carriers
w	Space-charge-region width
ω	Angular frequency
X^2	Least square
$x_{n,p}$	Space-charge-region edges
χ	Electron affinity
ξ	Energy difference between Fermi level and valence band maximum

Physical constants

q	$1.602 \cdot 10^{-19}$ C	Elementary charge
ε_0	$8.854 \cdot 10^{-12}$ F/m	Permittivity in vacuum
m_0	$9.11 \cdot 10^{-31}$ kg	Electron rest mass
h	$6.626 \cdot 10^{-34}$ J·s	Planck constant
k	$1.381 \cdot 10^{-23}$ J/K	Boltzmann constant
c	$2.998 \cdot 10^{8}$ m/s	Speed of light in vacuum