

Abbreviations

CCSVT	Chemical Closed- Space Vapor Transport
CBM	Conduction Band Minimum
CVT	Chemical Vapor Transport
CSVT	Close- space Vapor Transport
DAP	Donor- Acceptor Pair recombination
EDX	Energy Dispersive X-ray analysis
ERDA	Elastic Recoil Detection Analysis
ESR	Electron Spin Resonance
FB	Free-to-Bound transitions
FE	Free Exciton
FFT	Fast Fourier Transformation
FWHM	Full Width at one Half of the Maximum
GI- XRD	Grazing incidence X ray Diffraction
JCPDS	Joint Comittee on the Powder Diffraction Spectra
LO	Longitudinal Optical photon
PL	Photoluminescence
PVD	Physical Vapor Deposition
TEM	Transmission Electron Microscopy
SNMS	Secondary Neutral Mass Spectroscopy
SLG	Soda Lime Glass
SRIM	Stopping and Range of Ions in Matter
RTP	Rapid Thermal Process
UV- PL	Ultra- Violet Photoluminescence
VBM	Valence Band Maximum
XRD	X ray Diffraction
XRF	X- ray Fluorensence Analysis
ZSW	Zentrum für Solarenergie und Wasserstoff Forschung Stuttgart Germany.

List of figures

1. **Figure i.1.** *Solar radiation by regions of the world with higher energy potential in the whites areas* (From ref [2])
2. **Figure 1.1.** Theoretical predicted efficiencies of various single junction cells based semiconductors under AM. 1.5 illumination.
3. **Figure 1.2:** Unit cell CuGaSe₂ Chalcopyrite structure in the tetragonal D_{2d}^{12} space group, where the a and b directions are equivalent ($a = b = 0.5619$) and the c axis being different ($c = 1.1026$).
4. **Figure 1.3.** Cu₂Se - Ga₂Se₃ pseudobinary diagram for temperatures $T > 800$ °C at 1atm.
5. **Figure 1.4.** Schematic band structure and selection rules for the zinc blende (ZB) and chalcopyrite structures showing crystal field and spin-orbit splitting of the valence band. Three different bandgaps ($E_0(A)$, $E_0(B)$, $E_0(C)$) are shown.
6. **Figure 1.5** The formation the of the ($2V_{Cu}^-$, Ga_{Cu}^{2+}) defects in chalcopyrites compounds.
7. **Figure 1.6:** Schematic representation of the perturbed band and impurity states in the presence of potential fluctuations. An electron captured at a donor defect state tends to recombine with holes at the closest neutral acceptor states giving rise to direct transitions i) and ii). The carriers, prior to recombination could also tunnel to the closet well by indirect recombination with lower photon energy emission, thus reducing the energy of the transition iii).
8. **Figure 3.1.** Basic feature of the chemical close-space vapor transport (CCSVT) system used to grow CuGaSe₂ thin films.
9. **Figure 3.2.** Source and substrate temperature vs. process time including all steps in the CuGaSe₂ thin film growth by CCSVT. Q_{H_2} and Q_{HCl} are H₂ and HCl quantities, respectively.
10. **Figure 3.3.** The evolution of CuGaSe₂ (a) film thickness and (b) [Ga]/[Cu] ratio as a function of growth time, t_{g2} , in the second stage of the CCSVT process.

11. **Figure 3.4.** XRD diffractograms of the CuGaSe₂ thin films grown on Mo/SLG substrates as a function of the growth time t_{g_2} in the second CCSVT stage. All other process parameters are kept constant, as indicated in Figure 2. The lines and symbols mark the CuGaSe₂, Cu₂Se and Mo peak positions according to JCPDS data.
12. **Figure 3.5 :** GI-XRD measurements performed at incident angles of 1° and 0.3°. The lines and symbols mark the CuGaSe₂ peak positions according to JCPDS data.
13. **Figure 3.6.** Top view (a) and cross-sectional (b) scanning electron microscopy (SEM) images for the CuGaSe₂ thin film grown on Mo/SLG substrate having a composition of $[\text{Ga}]/[\text{Cu}] = 1.11$, corresponding to the second growth time, t_{g_2} , of 11 min.
14. **Figure 4.1.** Square of absorption coefficient versus photon energy measured on CCSVT-grown CuGaSe₂ thin films with different $[\text{Ga}]/[\text{Cu}]$ ratio according to the table 3.1 of the chapter 3. There are three fundamental optical absorption at 1.67eV, 1.75eV and 1.93eV.
15. **Figure 4.2.** The energy transitions $E_0(\text{A})$, $E_0(\text{B})$, and $E_0(\text{C})$ at the fundamental absorption edge of CuGaSe₂ thin films with varying the $[\text{Ga}]/[\text{Cu}]$ ratio at room temperature. $E_0(\text{A})$ and $E_0(\text{B})$ transitions related to the crystal-field-split gap, while the higher energy $E_0(\text{C})$ transition corresponds to the spin-orbit-split gap. The open symbols represent measured the data extracted from the $\alpha^2 = f(h\nu)$ curves in Figure 4.1, and the full symbols display the reported values from literature [65].
16. **Figure 4.3.** (a) TEM cross-section of a CuGaSe₂/Mo/SLG structure having a composition of $[\text{Ga}]/[\text{Cu}]=1.11$. Labels identify different layers of the heterostructure. (b) TEM micrograph of the polycrystalline CuGaSe₂ film involving a grain boundary between two crystallites. The inset shows an electron diffraction pattern of a CuGaSe₂ crystallite, proving its high crystalline quality. (c) Enlarged TEM micrograph of the CuGaSe₂/Mo interface - (point B in Figure 1a).
17. **Figure 4.4.** EDX spectrum of the point (A) in the middle of the CuGaSe₂ thin film and (B) at the CuGaSe₂/Mo interface. The points A and B are correspond to regions A and B in Figure 4.3a, respectively. The insets show the calculated concentrations of the corresponding elements.
18. **Figure 4.5 :** ERDA depth profile of elemental concentrations of the CuGaSe₂ thin films on Mo/SLG substrates with the ratios of (a) $[\text{Ga}]/[\text{Cu}] = 1.11$ and (b) $[\text{Ga}]/[\text{Cu}]$

= 1.26. The lines depict guides to the eye. The averaged elemental concentrations are inserted in the inset.

19. **Figure 5.1:** Simulated Ge atom distribution profile in CuGaSe_2 (solid line) after 50, 150, 200 keV implantation with Ge ions respectively, and (dashed line) same amount of Ge ions for each energy but with individual implantation. The distribution is computed without diffusions effects (thermal diffusion) and without sputtering effects (surface roughing and etching).
20. **Figure 5.2.:** Depth profile of Ge implanted ions into CuGaSe_2 thin films for the three set of samples (samples #1,#2,#3(table 5.1)) characterized by secondary neutral mass spectroscopy (SNMS).
21. **Figure 5.3:** Radiative recombination model of CuGaSe_2 of CuGaSe_2 from Bauchknecht et al.
22. **Figure 5.4:** Radiative recombination model of CuGaSe_2 of CuGaSe_2 from Meeder et al.
23. **Figure 5.5:** Radiative recombination model of CuGaSe_2 from Susanne et al
24. **Figure 5.6:** Photoluminescence spectra of polycrystalline CuGaSe_2 thin films on Mo coated soda lime glass as a function of $[\text{Ga}]/[\text{Cu}]$ ratio at $T = 10\text{K}$ and $P_{exc} = 50 \text{ mW}$.
25. **Figure 5.7:** PL spectra of stoichiometric polycrystalline CuGaSe_2 thin films at $T = 10\text{K}$ and $P_{exc} = 50 \text{ mW}$. The inset represents the Gaussian fit of the PL peak structure between 1.6 and 1.7 eV.
26. **Figure 5.8:** Fit of equation 5.4 to experimental data for the D1A1 (a) and D1A4 (b) photoluminescence peak in CCSVT prepared CuGaSe_2 . The line represents the fitting with parameters $h\nu_\infty$ and $h\nu_B$.
27. **Figure 5.9.:** Logarithmic photoluminescence spectra of the top (full triangles) and back (open circles) sides of the CuGaSe_2 thin films on SLG substrates as a function of $[\text{Ga}]/[\text{Cu}]$ ratio. ($T = 10 \text{ K}$, $\lambda = 514.5 \text{ nm}$, $P_{exc} = 20 \text{ mW}$).
28. **Figure 5.10:** Photoluminescence maximum (PLM) of the shallow defect emission (D1A1) of the top and back sides as a function of $[\text{Ga}]/[\text{Cu}]$ ratio. The inset represents the difference between the D1A1 PL maximums of the both sides.

29. **Figure 5.11:** Visible and UV- PL spectra of CuGaSe₂ thin films exhibiting a red-shift of ~ 13 meV of the Vis PL spectra due the higher surface sensitivity of the UV- PL. (@ 10 K and $P_{exc} = 20$ mW). The UV-PL spectrum is normalized by a factor 2.6.
30. **Figure 5.12:** Compared PL spectra of Ge implanted using three kinetic energies, as-grown and implanted, and as-grown films at 10 K and 20mW measured with the visible line (514 nm) of the laser.
31. **Figure 5.13:** Dependence of PL intensity with excitation intensity of the Ge-implantation related 1.67eV peak emission C at 10 K.
32. **Figure 5.14:** *PL spectra of the Ge- Implanted CuGaSe₂ thin films using three kinetic energies, at 10 K and 20mW using two different excitation line of the Ar⁺ laser at 351.1 nm and 514 nm. The UV spectrum is normalized by a 9.83 factor.*
33. **Figure 5.15:** (a) PL intensity dependence on excitation for the A and B transition lines at 10K, and (b) Fitting of the Dependence of PL intensity with excitation intensity density P_{exc} / P_{max} using equation 5.7. The k values are determined from the equation 5.7 fit lines
34. **Figure 5.16:** Photoluminescence of as grown and Ge doped CuGaSe₂ (sample #1,#2,#3) as function of Ge atomic concentration(T=10K, $\lambda = 351.1$ nm, Power excitation of the laser P = 20mW).
35. **Figure 5.17:** (a) Temperature dependence of the UV luminescence of the Ge implanted CuGaSe₂ films (sample 3#) and (b) temperature dependence of the integrated intensity of the 1.47 eV emission. The curves displays the results of parameters fitting to equation 5.8 in the temperature range of 10 to 300 K, where the ionization energy is estimated to be $E_{act} = 57 \pm 5$ meV. ($\lambda = 351.1$ nm, Power excitation of the laser P = 20mW).
36. **Figure 5.18:** Fit of equation 5.4 to experimental data for the emission line at 1.47 eV in Ge implanted CuGaSe₂ films. The line represents the fitting parameters $h\nu_{\infty}$ and $h\nu_B$.
37. **Figure 6.1:** ESR spectra of as-grown; as-grown and annealed; Ge implanted and annealed CuGaSe₂ thin films all taken at T=5K. It is clearly noticeable that a new ESR signal appears at $g = 2.003$ for Ge implanted samples.

38. **Figure 6.2:** ESR signal at $g = 2.003$ measured at $T = 5\text{K}$. The solid line is the result of fitting with the first derivative of Lorentzian function.
39. **Figure 6.3:** Temperature dependence of the normalized paramagnetic susceptibility χ_0 of Ge implanted CuGaSe_2 films for different Ge concentration as indicated in the figure. The solid line is fit assuming Curie type susceptibility.
40. **Figure 6.4 :** (a) Ge concentration dependence of the ESR signal at $g = 2.003$ and $T = 5\text{K}$. (b) spin number determined from the ESR spectra at $T = 5\text{K}$ as a function of Ge atoms. The error bars indicates the relative uncertainties.

List of tables

1. **Table 3.1 :** Survey of the CuGaSe₂ films prepared by the CCSVT deposition technique with their corresponding deposition parameters, composition and thickness.
2. **Table 5.1:** Implantation conditions.
3. **Table 5.2:** Energy and FWHM of the two Gaussian peaks of the figure 5.5.
4. **Table 5.3:** Fitting parameters hv_∞ , hv_B and the sum of the ionization energies of donor and acceptor levels $E_A + E_D$ is derived from the equation 5.3 with the band gap at T = 5K, being $E_g = 1.73$ eV. Bohr radius R_B are determined using fitting parameters. ^{1,2} References to which the ionization energies $E_A + E_D$ are compared.
5. **Table 5.4:** Fitting parameters hv_∞ , hv_B and the sum of the ionization energies of donor and acceptor levels $E_A + E_D$ is derived from the equation 5.3 with the band gap at T = 10K, being $E_g = 1.73$ eV.
6. **Table 6.1:** Possible Ge occupation on the CuGaSe₂ sites and the resulting electron configuration and paramagnetism activity.
7. **Table 6.2:** Narrow ESR signal ranging from 2.002-2.006, observed for chalcopyrite compounds and ZnSe.