Chapter 7
Summary and outlook

7.1 Summary

This chapter is devoted to the final highlight where this work has substantially contributed to the understanding of the $CuGaSe_2$ thin film semiconductor physics and deposition technology. The study has been carried out into three directions: The preparation of single phase $CuGaSe_2$ thin films by the chemical closed- space vapor transport (CCSVT) deposition technique, the characterization of the structural and optical properties of the as- grown $CuGaSe_2$ films, and finally the investigation of Ge doping on the $CuGaSe_2$ thin films prepared by CCSVT.

- A novel chemical closed- space vapor transport (CCSVT) technique has been developed for the growth of single phase $CuGaSe_2$ thin films using two growth stages. The Ga_2Se_3 employed as source material was stoichiometrically volatilized at 550°C by a controlled amount of HCl/H_2 agent at a fixed pressure. Cu precursors deposited on clean or Mo-coated soda lime glass (SLG) substrates were thermally and chemically treated under gaseous $GaCl_x/H_2Se$ atmosphere in the CCSVT cell. Cu deposited on the SLG substrate reacts with the volatilized gas phase compounds of Ga_2Se_3 and $CuGaSe_2$ films were prepared with a growth rate of 230 - 240 nm/min by using a single stage process. After the first growth stage the major hurdle encountered is that no correlation between $CuGaSe_2$ films properties (thickness and composition) could be realized because of their non- reproducibility for the same growth parameters. In order to overcome this hurdle, an additional second stage process was applied with a growth rate spanning 10 to 60 nm/min, for the fine tuning of the $CuGaSe_2$ composition and electronic properties. Therefore, a film property-growth parameters relationship was found.
- Single phase polycrystalline thin films of $CuGaSe_2$ in the compositional range of $1.0 \leq [Ga]/[Cu] \leq 1.3$, corresponding to a thickness ranging from 1.6 μm to 1.9 μm deposited onto plain or Mo- coated soda lime glass (SLG) were prepared and found to be polycrystalline with a strongly preferred <221> orientation. A combination of microstructural investigations of the films by TEM, EDX within the TEM and ERDA measurements has shown that $CuGaSe_2$ thin films possess high crystalline bulk quality with Cu, Ga and Se homogeneously distributed within the $CuGaSe_2$ bulk. One of the main result of this

present work was found to be the accumulation of Ga in the region of the $CuGaSe_2$/Mo interface and the dependence of the $CuGaSe_2$ surface composition on the integral [Ga]/[Cu] ratio in the film, namely Ga- and Cu- poor, Se- rich surface for stoichiometric films; and Cu- poor, and Ga- and Se- rich surface for increasing [Ga]/[Cu] ratios. These observations were also supported by optical measurements carried out through photoluminescence and absorption measurements.

- In order to gain a better understanding of the influence of the extrinsic doping of the $CuGaSe_2$ films and why many attempts towards the type inversion in the p- type $CuGaSe_2$ compounds by varying the composition or by doping with extrinsic defects have failed, ion implantation was used to introduce Ge into $CuGaSe_2$. Photoluminescence of the Ge containing films has evidenced the presence of new defects such as donor levels in the band gap. Electron spin resonance measurements of the Ge- containing $CuGaSe_2$ films has highlighted an additional ESR resonance observed at $g = 2.003$ ascribed to donors. However, Curie paramagnetism up to room temperature for all the Ge implanted films, characteristic of localized states has been observed for this resonance. This was an indication that donor electrons are electrically inactive even at room temperature because the ESR signal at $g = 2.003$ is observed without change of the ESR line shape in the whole temperature range investigated. An explanation was that these donor electrons either remain bound to donors or they are trapped by a deep defect.

It can be summarized in the present thesis that high quality $CuGaSe_2$ films with good and reproducible growth parameters - film properties can be achieved using the CCSVT process. Extrinsic doping of CCSVT- grown $CuGaSe_2$ films with Ge via ion implantation has given rise to new defects (ESR and PL). Interestingly, we can cite the new donor levels that are not electrical active within the band gap of the implanted films. For the first time, the electrically inactivity of the donors found in $CuGaSe_2$ films after Ge implantation were highlighted and can explain the difficulties encountered to dope $CuGaSe_2$ compounds.

7.2 Suggestions for future investigations

In the future, the exploitation of effects of doping will most likely allow further enhancements of the efficiencies of $CuGaSe_2$ devices. Another interesting subject to explore will be the understanding of firstly the electrically inactivity of the donors in the doped films, secondly the broadening of photoluminescence and absorption spectra occurring for Ga- rich films with the overall defect density and finally the local bonding situation of incorporated Ge atoms in the host lattice of chalcopyrite. Extrinsic doping using elements other than Ge is also necessary.