

Summary and Conclusions

Up to now device performance of thin film solar cells based on CuInS_2 is limited by an open circuit voltage V_{oc} still significantly below the limit calculated theoretically for an ideal solar cell with a band gap of 1.5 eV. The incorporation of isovalent and non-isovalent substitutions offers the possibility of deliberately influencing and improving the electronic and structural properties of chalcopyrite thin films.

The major focus of this work was the investigation of effects of the incorporation of gallium into CuInS_2 chalcopyrite thin films which serve as absorber layers in thin film solar cells. The influence of Ga-incorporation onto the thin film growth in a two step process, onto the structural properties of the film, and onto the device parameters of the related solar cells have been investigated. Due to the advantages of a simple two step process this work has mainly considered $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ thin film samples prepared sequentially from metallic precursors by reactive annealing in sulfur vapor or $\text{H}_2\text{S}/\text{Ar}$. The amount of copper in the precursor was always over-stoichiometric.

Perhaps the most significant result of this work is the experimental evidence that the substitution of indium in CuInS_2 thin films by small amounts of the isovalent gallium is one way to substantially increase V_{oc} . Open circuit voltage values well above 800 mV were obtained. Unlike previously described methods used to enhance V_{oc} in solar cells based on CuInS_2 gallium incorporation up to a certain amount ($[\text{Ga}]/([\text{In}] + [\text{Ga}]) < 0.3$) did not induce a more voltage dependent photocurrent, i.e. the fill factor could be maintained at 70 %.

An investigation of the reaction kinetics and the phase formation during film growth in rapid thermal furnaces revealed major differences in the reaction path of CuInS_2 and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ absorber layers, i.e. delayed sulfurization, indirect sulfur incorporation and the preferred segregation of CuGaS_2 . The combination of quenching experiments with depth-resolved Raman investigations and XRD-measurements in asymmetric mode allowed to derive a model for the growth process of Ga-free and Ga-containing CuInS_2 thin films, according to which the process can roughly be divided into three steps.

Precursor alloying: Cu-In alloying was found to be strongly suppressed by the presence of gallium in the precursor stack. An investigation of inter-metallic phase formation in Cu-In and Cu-(In,Ga) precursors after deposition and after several storage intervals revealed that a CuGa_2 phase, which acts as a diffusion barrier at the Cu/(In,Ga) interface, is the reason for the absence of Cu-In binaries in Ga-containing precursors.

Incorporation of sulfur: In the presence of gallium chalcopyrite formation shifts to higher temperatures and/or later stages of the sulfurization process. A phase analysis of samples

quenched at different stages of the sulfurization process showed that in the Ga-free case the chalcopyrite phase grows directly from Cu-In alloys. However, in the case of reactive annealing of Cu-(In,Ga) precursors the growth path is more indirect and involves the formation of an intermediate In-rich CuIn_5S_8 phase, thereby delaying the formation of the ternary chalcopyrite. The shift from a direct to an indirect growth process are caused by different inter-metallic phases in the respective precursors. Another feature, commonly reported for $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ -based chalcopyrite thin films sequentially processed from Cu-In-Ga precursors, is a very inhomogeneous Ga-depth distribution, where almost all gallium accumulates close to the Mo-back contact. It could be shown here that such a segregation behavior of Ga is also typical for the sequential preparation of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ thin films. In contrast to earlier explanations of the effect which assume a slower reaction rate of CuGaSe_2 with respect to CuInSe_2 , depth-resolved Raman measurements revealed that in the case of the CuInS_2 - CuGaS_2 alloy system the inhomogeneous depth distribution is due to the preferred segregation of CuGaS_2 at the stage of ternary compound formation. Once all the gallium in the precursor is used up a CuInS_2 layer overgrows the CuGaS_2 , thereby leading to a bilayer structure of the sulfurized film with a phase close to CuGaS_2 at the bottom and a phase close to CuInS_2 at the surface of the film. The segregation of CuInS_2 at the surface of the already formed CuGaS_2 layer furthermore indicates that the incorporation of sulfur in such a sequential process always takes place at the top of the layer. Assuming that the reaction kinetics in the thin film are mainly governed by reactive diffusion the finding is in good agreement with literature values of cation and anion diffusion in ternary chalcopyrites.

Recrystallization: After the ternary compounds have formed ongoing annealing causes a recrystallization process which is accompanied by an increase in grain size and a clear improvement of the structural quality of the film. The latter could best be shown by analyzing the X-ray diffraction intensity of the chalcopyrite super lattice peaks of the layer and comparing the experimental results with simulated values expected for a thin film of perfect chalcopyrite ordering. The presence of the secondary copper-sulfide phase, which forms during film growth due to the over-stoichiometric amount of copper in the precursor, was found to be crucial for the appearance of the typical cation ordering of the chalcopyrite lattice. There is a direct correlation between the amount of copper-sulfide present during film growth and the intensity of the chalcopyrite super lattice peaks which are a good indicator of the cation ordering in the film. A tentative explanation based on a model of a moving Cu_{2-x}S grain boundary was proposed as the underlying mechanism for the observed film recrystallization.

During the recrystallization stage of the film growth process gallium from the phase at the bottom and indium from the phase at the top inter-diffuse. The degree of alloying of the resulting quaternary $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ phases strongly depends on annealing temperature and time. The decisive role of short circuit paths of high diffusivity was clearly observed in annealing experiments performed with $\text{CuInS}_2/\text{CuGaS}_2$ diffusion couples. Again, the presence of the copper-sulfide phase has a large impact on the effectiveness of the inter-diffusion process which underlines the role of the secondary phase as a high mobility path for cations. This appears to be due to cation vacancies in the Cu_{2-x}S copper-sulfide phase

which offer diffusion paths in a structure which is otherwise very similar to the chalcopyrite structure of the CuInS_2 phase. In order to describe the inter-diffusion process and the associated Ga-depth profile a numerical simulation of the XRD-spectra of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ thin films was realized in the course of this work, and was then combined with a 2-dimensional diffusion model that accounted for bulk and grain boundary diffusion. This approach allowed for a quantitative determination of the respective diffusion coefficients with great accuracy and independent of resolution limits of destructive profiling techniques.

As already mentioned the presence of Ga in the CuInS_2 absorber layers leads to a very systematic increase in open circuit voltage V_{oc} of the corresponding solar cells. It has been shown earlier that the conduction band exhibits a cliff at the $\text{CuInS}_2/\text{CdS}$ interface and that the corresponding heterojunction solar cells are limited by interface recombination. As a consequence the attainable open circuit voltage does not only depend on the absorber band gap but also on the specific band line up at the interface. A discussion of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2/\text{CdS}$ interface band line up as a function of the band gap of the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ absorber indicates that an increase in band gap can be utilized in order to increase V_{oc} . This agrees well with the strong experimental correlation between annealing temperature and time and the observed open circuit voltage, since the diffusion controlled Ga-alloying of the CuInS_2 top phase, leads to a widening of the absorber band gap, as indicated by spectral response measurements. However, the Ga-induced gain in V_{oc} was found to be higher than expected from the shift in the absorber band gap. Based on the grain boundary diffusion model, which was already successfully employed to describe the Ga-depth profile, it has to be concluded that the effect is related to a localized band gap widening at the absorber surface, due to copper-sulfide assisted surface diffusion of gallium.

In conclusion the experimental tools and the models developed in this work allowed for a profound understanding of the sequential growth process of CuInS_2 thin films and for the identification of grain boundary diffusion as the determining factor for the incorporation of Ga in CuInS_2 thin films and the resulting Ga-depth profile. The observed correlation of Ga-alloying, absorber band gap and open-circuit voltage enhancement without fill factor loss provides significant flexibility in adapting a CuInS_2 -based solar cell to a given application. The interaction between diffusion mechanisms in the grain boundaries and in the bulk will require further investigation and may perhaps be utilized to deliberately improve the electrical properties of the heterojunction by means of Ga-induced band gap engineering in the near interface region of the heterojunction. An exact quantification of Ga-induced changes of the recombination in the heterojunction, especially with respect to the barrier height, and its dependence on the amount of Ga-alloying is also highly desirable with respect to fully exploit the potential of gallium incorporation in a CuInS_2 -based solar cell.

