Introduction and Outline

The limited resources of conventional and nonrenewable energy sources such as gas, coal and petroleum and the growing opposition to nuclear power generation, motivated by concerns about safety issues and radioactive waste disposal, have led to an increasing demand for safer, cleaner, and most importantly renewable sources of energy. Photovoltaic devices offer such a solution and have already been used for over three decades; initially for power generation on satellites and space crafts and later also for terrestrial applications. The first solar cells where based on crystalline silicon wafers and today's mass production of photovoltaic modules still mainly uses this established and reliable technology. However, due to the high material and production costs of crystalline silicon, prices for photovoltaic power generation are not competitive in most urban areas where conventionally generated power is readily available. Thin film technologies present an interesting alternative to the silicon technology since they rely on the deposition of highly absorbing materials, which allow for photo active layers of a few micrometer thickness, and they can be produced by economical, high-volume manufacturing techniques. Presently, several manufacturing facilities based on a-Si, CdTe and CuInSe$_2$ are in the pilot-line stage. Latest developments in the field of thin film solar cells have been reviewed recently [1, 2].

In contrast to the conventional homojunction silicon solar cell, where a p-n junction is achieved by diffusion of a dopant into a moderately doped silicon wafer, most thin film solar cells are heterojunction devices. The heterojunction structure consists of at least two different semiconductor materials, one p-type and one n-type. Photon collection and charge carrier generation mainly occurs in one material (the p-absorber), whereas the other material is transparent and only needed to form a p-n junction. The design has inherent advantages with respect to the required carrier lifetimes at the cell surface and in the bulk of the material. In comparison to a heterojunction, the carrier generation maximum is moved away from the surface to the junction where carrier collection is assisted by the built-in field of the diode.

Hetero-junction solar cells based on Cu-chalcopyrite (I-III-VI$_2$ compounds) absorber layers are a proven basis for photovoltaic devices. Typical absorber materials are CuInSe$_2$, CuInS$_2$, CuGaSe$_2$ and their alloys with band gaps ranging from 1.05 eV to 1.7 eV. The high absorption coefficient of these materials assures absorption of the entire incident photon flux in an absorber layer as thin as a few microns. Polycrystalline chalcopyrite based thin film solar cells have reached conversion efficiencies as high as 18.8 % [3]. This is the highest value so far reached for any polycrystalline thin film solar cell. This record device was based on a Cu(In$_{1-x}$Ga$_x$)Se$_2$ absorber layer prepared by coevaporation of the elements and a CdS/ZnO window layer.

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Despite the tremendous progress made, until recently the understanding of fundamental physical properties of the semiconductor materials constituting the hetero-junction has been rather limited, when compared to the general knowledge base available for classical semiconductors such as silicon. Device development has often been driven by empirical work or as Rau [4] puts it briefly: "it worked first, and was explained later". More recently, there has been increasing insight into the properties of the absorber/window interface [5], the current transport and the recombination processes in chalcopyrite heterojunction devices [4, 6, 7]. Furthermore, a better understanding of the band and lattice structure of these ternary compounds and their alloys was achieved by theoretical band structure calculations [8, 9]. Up to now most of the experimental efforts have been focused on $CuInSe_2$ and the $CuInSe_2$-$CuGaSe_2$ alloy system.

This work investigates $CuInS_2$ and alloys of the $CuInS_2$-$CuGaS_2$ system. When compared to other I-III-VI$_2$ materials, $CuInS_2$ has several advantages, e.g., its electronic band gap is ideally suited for series connection of single solar cells, it is well matched to the solar spectrum, and its environmental impact is relatively low (Se-free). The best $CuInS_2$-based solar cells reported so far have efficiencies up to $12.7\,\%$ [10, 11]. However, device performance is currently limited by an open circuit voltage V_{oc} significantly below the theoretical limit calculated for an ideal solar cell with a band gap of 1.5 eV [12]. So far, this limitation was found to be inherent to the material as several deposition techniques led to similar device performances. It is well known that characteristic material properties of ternary I-III-VI$_2$ compounds, such as lattice constants, band gaps and defect chemistry can be controlled by adjusting the concentration of isovalent substituents resulting in quaternary (e.g. $Cu(In,Ga)Se_2$) or even penternary compounds (e.g. $Cu(In,Ga)(S,Se)_2$). Current thin film record devices are achieved by substituting In partially by Ga in a $CuInSe_2$ based absorber layer, which leads to a shift in the band gap that better matches the solar spectrum and to higher open circuit voltages. Although the possibility of engineering the band gap of $CuInSe_2$ absorber layers by adjusting the Ga-concentration has been known for more than a decade, first reports on the incorporation of Ga in $CuInS_2$ solar cell absorber layers, where a similar relation between band gap and Ga concentration exists, were published only recently [13, 14]. These preliminary data indicated the potential of the incorporation of small amounts of Ga to substantially increase V_{oc} and were the main motivation for a systematic study of the effects of Ga-incorporation in $CuInS_2$ thin films, as presented in this work. A profound understanding of Ga-alloying in $CuInS_2$ thin films is highly desired for ongoing device development, especially with respect to overcoming the open circuit voltage limitation of $CuInS_2$-based solar cells.

Outline

The specific aim of this work is the investigation of the incorporation of gallium into $CuInS_2$ thin films. This thesis focuses mainly on gallium induced changes in the thin film

growth process, the understanding of an In-Ga interdiffusion process which was found to occur in Ga-containing thin films and the analysis of the current-voltage characteristics of heterojunction solar cells processed from the Ga-containing CuInS$_2$ absorber layers.

This thesis is divided into the following chapters:

Chapter 1 starts with a brief discussion of I-III-VI$_2$ chalcopyrite compound semiconductors. The peculiarities of the chalcopyrite structure and their effects on the electronic band structure are outlined and experimental results concerning the CuInS$_2$-CuGaS$_2$ alloy system are briefly reviewed. A short introduction into thin film solar cells follows. The general design of a heterojunction solar cell, the device structure of the chalcopyrite solar cells investigated in this work, is presented. The dependence of the open circuit voltage on the band gap of the absorber is discussed with respect to the dominating recombination mechanism in the heterojunction diode.

A short description of the sequential preparation process for solar cells as used in this work is given in the beginning of **Chapter 2**. Thereafter, this chapter outlines experimental techniques employed in this work, i.e. depth profiling by secondary neutral atoms mass spectroscopy (SNMS), micro-Raman spectroscopy and X-ray diffraction. Aspects of these techniques specific to the analysis of chalcopyrite thin films are discussed. Several fundamental aspects of X-ray scattering are discussed in order to explain numerical calculations of X-ray diffraction spectra of chalcopyrite thin films with graded lattice constant. This calculation enables the use of X-ray diffraction for non-destructive depth profiling.

Chapter 3 investigates the growth of Cu(In$_{1-x}$Ga$_x$)S$_2$ thin films by annealing of metallic Cu-(In,Ga) precursors in a sulfur containing reactive atmosphere. The process has been divided into three stages, i.e, A) precursor alloying, B) the incorporation of sulfur, and C) film recrystallization, which are discussed in separate sections. Before discussing the experimental results the sections briefly consider the thermodynamical phase relations of the reacting species. The reaction kinetics and phase formation sequence have been investigated by means of depth-resolved Raman investigations and XRD-measurements in asymmetric mode. The strongly inhomogeneous Ga-depth distribution in Ga-containing absorber films, as observed in SNMS sputter depth profiles, is explained by the observed phase formation sequence. Furthermore, a tentative explanation for the observed improvement in morphological grain size and chalcopyrite cation ordering in the course of the sulfurization process is proposed. The experimental results are summarized in a model of the growth process. Since In-Ga interdiffusion has been found to determine the Ga-depth distribution in absorber layers, the diffusion process has been further investigated by annealing experiments with suitably designed CuGaS$_2$/CuInS$_2$ thin film diffusion couples in the temperature range from 500 °C to 600 °C. On the basis of a 2-dimensional interdiffusion model, which includes rapid diffusion along grain boundaries, chemical diffusion coefficients for In in CuGaS$_2$ and Ga in CuInS$_2$ thin films have been derived by numerical fits of calculated XRD-spectra to the experimental data.

Chapter 4 reports on heterojunction solar cells based on Cu(In$_{1-x}$Ga$_x$)S$_2$ absorber layers processed in the course of this work. After a brief review of earlier works related to CuInS$_2$-based thin film solar cells, the chapter discusses the j-V characteristics and the spectral response of the short circuit current of Cu(In$_{1-x}$Ga$_x$)S$_2$/CdS/ZnO-based solar cells. The

open circuit voltages V_{oc} of Ga-containing solar cells will be analyzed with respect to the absorber layer growth conditions and with respect to absorber band gap values deduced from the spectral response of the short circuit current. The obtained experimental correlations of open circuit voltage, Ga-alloying and absorber band gap will be discussed in the framework of the current understanding of the dominating recombination mechanism at the absorber/buffer interface and recent considerations about the $Cu(In_{1-x}Ga_x)S_2/CdS$ band line-up. Based on these considerations and the 2-dimensional grain-boundary diffusion model introduced in the previous chapter a model will be derived which explains the Ga-related gain in V_{oc}. Ga-induced changes in the spectral dependence of the short circuit current will be discussed within the framework of the derived model.

A brief outline of the effect of deviations from perfect cation ordering in $CuInS_2$ thin films onto superlattice reflections in XRD can be found in the **Appendix**. An analytical solution for thin film grain boundary diffusion, and the parameters used in the simulation of the XRD-spectra are also listed in the Appendix.