Chapter 1

Introduction

The world annual energy consumption is predicted to rise from today's 13 TWa to 30 TWa by 2050. At the same time, the world is faced with the two demanding issues of declining fossil reserves and climate change caused by artificially produced greenhouse gas emissions (e.g., CO_2) [IPCC '07; Slaoui '07]. Therefore, the G8-countries decided to reduce their greenhouse gas emissions by 50 % by 2050 [Welt '08].

In order to satisfy the increasing demand for energy and to reduce the emission of CO_2, new technologies - for supplying energy in general and generating electricity in particular - have to be developed. With about 125000 TW of solar power striking the earth at any time, photovoltaic energy conversion (PV) may be the renewable energy source with the capacity to provide a major fraction of the future energy needs [Slaoui '07].

In spite of its enormous potential, PV provided only 0.3 % of the electricity produced in Germany in 2006 [Siemer '07]. This small fraction is mainly due to the high cost of PV compared to coal-based electricity. Today, the total costs for commercial photovoltaic modules amount to about $3-$4/Wp[1]. Including transport and installation and assuming a 20-year lifetime, this corresponds to a price of about $0.25-0.65/kWh for the generated electricity depending on the local illumination at the place of installation. This exceeds the costs for coal-based electricity ($0.04/kWh) by a factor of about 10 [Slaoui '07]. However, feed-in-tariffs for PV-generated electricity in Germany and Japan led to the evolution of a rapidly growing PV market (70 % growth in global production in 2007), which produced solar cells corresponding to 4.28 GWp in 2007 [Hering '08]. In order to maintain these growth rates, which are needed to fulfill the future energy needs, and to become independent of subsidization, the costs for PV-generated electricity must be decreased to the level of coal-based electricity. Therefore, cost-reduction is the major criterion in the development of new technologies for solar cell preparation [Goetzberger '03].

At present, approximately 90 % of the solar cells produced are based on crystalline silicon [Hering '08]. Due to its indirect band gap, silicon absorbs impinging photons much less strongly than comparable direct semiconductors [Würfel '05]. Therefore, the use of direct semiconductors allows replacing the 200 μm thick silicon absorbers by semiconductor thin films of about 2 μm. Due to the small thickness of thin-film solar cell absorbers, the charge carriers diffuse only over short distances. Thus, shorter lifetimes of the charge carriers and a higher defect density can be accepted in these films compared to silicon absorbers. Therefore,

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[1] "Wp" stands for "Watt peak" and describes the power produced under perpendicular illumination with a standardized AM 1.5 [NREL '08] solar spectrum. 1 Wp corresponds to to 1000 W/m^2.

polycrystalline thin films can be used as absorbers in such devices. This allows for the use of fabrication processes which consume less energy and material than the growth of monocrystalline silicon wafers and thus offers a great potential for cost reduction. One of the most promising candidates for application as absorber materials is the group of copper-chalcopyrites of the $Cu(In,Ga)(S,Se)_2$ family. Of these materials, the highest theoretical conversion efficiency of about 30 % was predicted for $CuInS_2$ due to its direct bandgap of 1.5 eV [Henry '80; Blieske '97]. Even though $CuInS_2$-based solar cells only yield efficiencies of up to 11.4 % to date [Siemer '01], they are already produced commercially [Meyer '07].

In chalcopyrite-based thin-film solar cells, the pn-junction is formed by a stack of n^+-ZnO/ i-ZnO/n-CdS/p-$Cu(In,Ga)(S,Se)_2$ layers. Today, a combination of vacuum and non-vacuum processes is applied for the deposition of these layers in order to obtain an optimum performance of the resulting solar cells [Klaer '98; Siemer '01; Klaer '03]. This requires various transfer steps and expensive vacuum technology. Potentially, using non-vacuum processes for the deposition of all layers in the solar cells allows a further reduction in the production costs. However, the most critical issue in the development of suitable non-vacuum processes is attaining device efficiencies which are competitive with those of vacuum-based processes.

In recent years, various non-vacuum methods have been developed [Kaelin '04].One of these methods is the S*pray Ion Layer Gas Reaction* (Spray ILGAR), which has been applied successfully to replace the toxic CdS layer in highly efficient $ZnO/CdS/Cu(In,Ga)(S,Se)_2$ solar cells by In_2S_3 [Allsop_1 '05; Allsop_1 '06]. Extending the applicability of this method to the deposition of $CuInS_2$ absorber layers would offer a great potential for cost-reduction in the fabrication of thin-film solar cells, since it combines the advantages of non-vacuum processes with the inherent potential of the $CuInS_2$ material.

The specific aim of the present thesis is the development of a Spray ILGAR deposition process for $CuInS_2$ thin-film solar cell absorbers. Due to the wet-chemical approach of the Spray ILGAR process, more elements and phases are involved in the growth process of the thin film than in conventional coevaporation processes. Hence also the growth mechanism underlying the deposition process can be expected to be more complicated in the case of the Spray ILGAR process. However, the understanding of the growth mechanism is a prerequisite for the improvement of the processes. Therefore, this thesis, organized as follows, comprises the microstructural and chemical characterization of the deposited $CuInS_2$ thin films in order to deduce a growth model and evaluate the applicability of these films as absorbers in thin-film solar cells:

Chapter 2 starts with a brief discussion of the material properties of the group of chalcopyrite semiconductors in general and $CuInS_2$ in particular. Besides the properties of these materials, also those of binary copper and indium phases, which are relevant for the later results, are presented. Furthermore, a short overview of common deposition processes for chalcopyrite thin films is given. At the end of the chapter, the current status of the Spray ILGAR process is reviewed with a special emphasis on the obstacles which have to be overcome in order to enable the deposition of $CuInS_2$ thin films.

Chapter 3 outlines the implementation of a Spray ILGAR process for the deposition of $CuInS_2$ thin films. As a first step, the development of deposition process for $Cu_{2-x}S$ ($0 \leq x \leq 0.2$) thin films is described. In particular, the required properties of a suitable copper-containing spraying solution are considered. Afterwards, the deposition of $In_2(O,S)_3$ thin films using the same process is discussed. In the third part of this chapter, two different approaches for the

deposition of $CuInS_2$ thin films are evaluated. Firstly, the $CuInS_2$ thin films are prepared by annealing of $Cu_{2-x}S/In_2(O,S)_3$ bilayers in H_2S atmosphere. In a second approach, $CuInS_2$ thin films were prepared by applying the process developed for $Cu_{2-x}S$ deposition, but using mixed copper- and indium-containing solutions in the spray step of the process. Films prepared by both approaches are characterized with respect to composition and morphology in order to evaluate their applicability as solar cell absorbers.

Chapter 4 investigates the growth of Spray ILGAR $CuInS_2$ thin films, in order to deduce a model for the underlying growth mechanism. Therefore, the different phases that are deposited or formed during the various steps of the Spray ILGAR process are characterized separately. From these characterizations, the phase transformations and reactions which occur in the different process steps are identified. Initially, the physical fundamentals of diffusion processes are briefly discussed. Afterwards, the growth analysis starts with the investigation of the phases deposited during the spraying of the solution. Secondly, the sulfurization of these phases during the H_2S gassing is analyzed. For both process steps, growth models are proposed that explain the formation of the observed phases. In the third part of the chapter, the composition and phase distribution of the completed Spray ILGAR $CuInS_2$ thin films is analyzed. From these results, the diffusion paths of the different phases in the film are deduced. At the end of the chapter a complete growth model is proposed, which can explain all the experimental observations made in this chapter. Finally, the growth model is tested quantitatively by comparing the duration of the process steps to the possible diffusion lengths of the elements in the various matrices.

Chapter 5 describes the microstructural characterization of the Spray ILGAR $CuInS_2$ thin films by Raman spectroscopy. The chapter begins with a brief introduction to Raman spectroscopy and reviews the vibrational properties of $CuInS_2$. This is followed by a study of the distribution of the polytypes of $CuInS_2$ (chalcopyrite-type and CuAu I-type cation ordered $CuInS_2$) in the Spray ILGAR $CuInS_2$ thin films. This distribution is correlated to the degree of crystalline order that is present in the different regions of the films. Afterwards Raman spectroscopy is applied to investigate and identify a carbon-containing compound that was observed to be incorporated in the matrix of the films in chapter 4. At the end of chapter 5, the asymmetry of the A_1-Raman mode of chalcopyrite-type $CuInS_2$ thin films, which was observed in this thesis, is analyzed by fitting the Raman spectra numerically according to the so-called phonon confinement model. These fits enable the correlation of the Raman spectra to the density of crystallographic defects and to strain in the films.

Chapter 6 reports on $CuInS_2$-based thin-film solar cells, which have been prepared from Spray ILGAR $CuInS_2$ thin film absorbers. As a basis for the study of these solar cells, the physical background for heterojunction solar cells is provided at the beginning of the chapter. Afterwards, the performance of the devices is correlated to the film morphology and to the structural properties of the different regions of the films, which were presented in chapters 4 and 5, respectively. Thereby, the influence of the different regions on the photovoltaic behavior of the solar cells is discussed.

Chapter 7 summarizes the main results of this thesis and discusses some modifications of the Spray ILGAR process for the deposition of $CuInS_2$ thin films. The chapter closes with an outlook on further process modifications and experiments that appear to be helpful in order to improve the performance of Spray ILGAR $CuInS_2$-based solar cells and to verify the models proposed in this thesis.

The Appendix provides complimentary information for the discussions in the previous chapters. A summary of the deposition parameters of all investigated samples is given in Appendix I. The abbreviations and symbols used in this thesis are listed in Appendix II and III, respectively. In Appendix IV, the phase diagrams of the Cu-S and In-S material system are depicted, whilst Appendix V compiles all diffusion constants and the respective references used in this thesis. In Appendix VI the Mathcad fitting routine is given which was written in order to simulate the Raman spectra in chapter 5. The analysis techniques which were applied in this thesis are briefly introduced in Appendix VII. The input parameters for the simulations of the quantum efficiency curves presented in chapter 6 and the air mass 1.5 solar spectrum are given in Appendixes IIX and IX, respectively. Appendices X and XI contain thermodynamic data of various compounds and a visualization of relevant Raman modes, which are discussed in this thesis. The Appendix closes with a list of the publications produced in the course of this thesis.