

# Chapter 7

## Summary and Outlook

In order to develop solar energy into a widely used energy source compatible with other energy sources such as coal-based electricity, a further cost reduction of this technology is needed. Using vacuum-free potentially low-cost techniques for the manufacturing of solar cells may contribute to achieving this goal. One of these techniques is the Spray ILGAR method.

The Spray ILGAR process was modified in this thesis, so that it enabled the deposition of CuInS<sub>2</sub> thin films at a deposition rate of up to 30 nm/min. In this form, the process could be used for the deposition of CuInS<sub>2</sub> absorber layers for thin-film solar cells for the first time.

In this process, the deposition of CuInS<sub>2</sub> thin films proceeds in the following steps:

1. Deposition of a precursor layer consisting of In<sub>2</sub>O<sub>3</sub> and copper by spraying of an InCl<sub>3</sub>/Cu(hfac)<sub>2</sub>/acetone solution
2. Complete sulfurization of copper to Cu<sub>2-x</sub>S (0 ≤ x ≤ 0.2) and partial sulfurization of In<sub>2</sub>O<sub>3</sub> to In<sub>2</sub>S<sub>3</sub>, which subsequently completely reacts with Cu<sub>2-x</sub>S to CuInS<sub>2</sub>.
3. Cyclic repetition of steps 1.-2.
4. Completion of the sulfurization by a post-deposition annealing in Ar/H<sub>2</sub>S atmosphere.

The microscopic characterization of the Spray ILGAR CuInS<sub>2</sub> thin films revealed a peculiar morphology of the films consisting of two differently crystallized regions: The lower part of the films at the molybdenum substrate is composed of a stack of about 30 nm thin CuInS<sub>2</sub> layers separated by carbon-containing interlayers of about 10 nm thickness (*layered bottom layer*). In contrast, the upper part of the films is formed by a *well-crystallized top layer* with grain sizes of 100-1000 nm (chapter 3).

To elucidate the origin of this bilayered growth mode was one of the main goals of this thesis. For the investigation of the growth mechanism, the phases and compounds which are formed at each step of the Spray ILGAR process were identified and characterized separately (chapter 4). Furthermore, the spatial distribution of Cu<sub>2-x</sub>S, CuInS<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> in the Spray ILGAR CuInS<sub>2</sub> thin films was ascertained. By evaluating the diffusion lengths of copper, indium, sulfur and oxygen in the respective media, diffusion processes were proposed, which determine the film growth. In conclusion, the investigations of chapter 4 allowed for the deduction of a growth model suggesting that the formation of the *layered bottom layer* and the *well-crystallized top layer* during the growth of the Spray ILGAR CuInS<sub>2</sub> thin films is caused by two different processes:

1. The deposition processes of In<sub>2</sub>O<sub>3</sub> and copper both depend on the availability of small amounts of H<sub>2</sub>O in the spraying solution. This H<sub>2</sub>O is provided either by the hydrated Cu(hfac)<sub>2</sub> compound or trace amounts of H<sub>2</sub>O in the acetone. In the In<sub>2</sub>O<sub>3</sub> deposition process, H<sub>2</sub>O is consumed by the hydrolysis of InCl<sub>3</sub>, whilst it is needed for the removal of adsorbed hfac groups in the copper deposition process. If both

processes occur simultaneously, they compete for the available  $\text{H}_2\text{O}$ . This leads to the incomplete removal of the hfac groups that are then incorporated into the film matrix as the carbon-containing interlayers in the *layered bottom layer*.

2. The formation of the *well-crystallized top layer* could be explained by the diffusion of indium into  $\text{Cu}_{2-x}\text{S}$  agglomerates on the film surface during the post-deposition  $\text{H}_2\text{S}$  annealing. These agglomerates have been formed previously during the Spray ILGAR process due to the fast diffusion of copper in  $\text{Cu}_{2-x}\text{S}$  and  $\text{CuInS}_2$ .

Based on the growth model deduced in chapter 4, the addition of  $\text{H}_2\text{O}$  to the spraying solution was predicted to prevent the layered morphology of the Spray ILGAR  $\text{CuInS}_2$  thin films. Preliminary experiments with  $\text{H}_2\text{O}$ -containing spraying solutions confirmed this prediction and thus provided a future recipe for the deposition of Spray ILGAR  $\text{CuInS}_2$  thin films.

The degree of crystalline order and phase purity in the  $\text{CuInS}_2$  domains of the *well-crystallized top layer* and the *layered bottom layer* of the Spray ILGAR  $\text{CuInS}_2$  thin films were investigated by means of Micro-Raman spectroscopy (chapter 5). These measurements revealed that the  $\text{CuInS}_2$  layers in the *layered bottom layer* contain two different modifications of  $\text{CuInS}_2$ ; the chalcopyrite and the CuAu-ordered phase. In contrast, the *well-crystallized top layer* was found to consist solely of chalcopyrite-type  $\text{CuInS}_2$ . Furthermore, the Raman studies for the first time revealed the dependence of the intensity of the  $E_{\text{LO}}^1$  and  $B_{\text{LO}}^1$  Raman modes of chalcopyrite-type  $\text{CuInS}_2$  on the phase purity of the probed material.

Raman spectroscopy also revealed that the carbon-containing interlayers in the *layered bottom layer* of the Spray ILGAR  $\text{CuInS}_2$  thin films consist of a blend of (nanocrystalline) graphite and amorphous carbon.

Additionally, the spectral distribution of the Raman  $A_1$  mode of chalcopyrite-type  $\text{CuInS}_2$  thin films was analyzed. This mode exhibits an asymmetric spectral distribution, which is known to be related to the efficiency of solar cells using such films as absorber layers. The spectral distribution of this mode was simulated numerically according to the *phonon confinement model*. These simulations yielded values for the average distances between crystallographic defects in the probed material, which confine phonons into nanocrystalline domains. These distances were of the order of 1-10 nm. In the course of this study, this model was extended, such that it also accounts for strains, which might be present in the probed  $\text{CuInS}_2$  films. All strains obtained from these simulations were tensile and lay in the range of 0.1-0.7 GPa, which agree well with previously published values. Complimentary TEM studies of the  $\text{CuInS}_2$  thin films led to the hypothesis that the phonon confinement may be caused by planar defects in the films.

Finally,  $\text{CuInS}_2$  thin films prepared by the Spray ILGAR method could be successfully applied as absorber layers in thin-film solar cells (chapter 6). These solar cells reached efficiencies of up to 4.1 % and thus proved the applicability of this method for solar cell absorber deposition. The analysis of the photovoltaic performance of these solar cells suggested that only those charge carriers contributed to the photocurrent of the cells, which were generated within the *well-crystallized top layer* of the absorber layer. However, maximizing the thickness of this layer did not result in an improved performance of the devices. This was assumed to be due to the creation of shunt paths in the *layered bottom layer*, whose porosity increases as the thickness of the *well-crystallized top layer* increases. Thus, the photovoltaic performance of the Spray ILGAR  $\text{CuInS}_2$ -based solar cells seems to be principally limited by their bilayered morphology.

In view of this limitation, the addition of  $\text{H}_2\text{O}$  to the spraying solution, which was shown to prevent this bilayered growth mode, can be considered to be a promising process modification in order to increase the efficiency of the devices in the future. Therefore, this thesis may

provide the basis for developing the Spray ILGAR process into a non-vacuum process for the manufacturing of efficient thin-film solar cells, which may contribute to a cost reduction of solar energy conversion.

