

## Chapter 6

### Summary and outlook

The open-tube chemical vapour deposition (CVD) technique, based on the chemical transport of elements in the form of volatile halide species from a source to a substrate induced by a temperature gradient, has been applied to the growth of thin films of CuGaSe<sub>2</sub> to be used as absorber films for photovoltaic (PV) applications. In this work, structural and compositional properties of such films, as well as the electronic performance of related devices, have been investigated as a function of the deposition conditions, in order to determine the limiting factors in the device operation associated with the growth method. On this basis, three different approaches to the optimisation of the film deposition for improved PV performance have been presented and assessed, including the realisation of lift-off devices, the growth of absorber films from Cu-precursors and the implementation of sequential deposition processes, leading in the latter case to improved figures of characteristic photovoltaic parameters in related devices.

The characterisation study has been carried out in two directions, including on one hand the analysis in the sub-micron scale of the structural properties of the films and their impact in subsequent device processing and operation, and on the other hand the electronic characterisation of complete devices, as a means of determining fundamental limiting factors in their performance. A convenient link between these two fields was provided by Kelvin probe force microscopy (KPFM), which has been shown in this work to be a suitable tool for the analysis of complex heterostructures characteristic of thin-film technologies.

A number of potential limitations related to material properties have been shown to affect the processing of CuGaSe<sub>2</sub> films based on single-stage CVD processes. The optimal single stage CVD deposition process represents a compromise between a preferable morphology, characteristic of slightly Cu-rich film compositions and characterised by large columnar grains and a reduced number of grain boundaries, and the electronic quality of the films, which in turn improves with slightly Ga-rich compositions. The high sensitivity shown by a number of CuGaSe<sub>2</sub> film properties to composition variations, as revised in this work, thus requires an extremely fine tuning in the single stage growth process in order to produce samples to be implemented in final devices. An issue of special importance regarding the composition dependence of film properties is the appearance of secondary phases during the growth of the chalcopyrite film. These phases have been identified as copper selenides, both stoichiometric Cu<sub>2</sub>Se and non-stoichiometric Cu<sub>2-x</sub>Se, and molybdenum diselenide 2H-MoSe<sub>2</sub>.

Copper selenide phases result from the little solubility of Cu excess into the chalcopyrite matrix, in agreement with reported phase diagrams and experimental results. In the case of CVD-grown samples, the growth under gaseous cation contents of  $[Ga]/[Cu](g) < 5$  leads to Cu-rich compositions in the solid phase of resulting films.

Various types of copper selenide phases have been identified, either forming entire crystallites among others of  $\text{CuGaSe}_2$  along the film thickness, segregating at surfaces and interfaces of  $\text{CuGaSe}_2$  crystallites, or as clusters embedded in the chalcopyrite matrix. Due to the nearly metallic character associated to these degenerated semiconductors, the presence of these secondary phases must be avoided in films to be processed as solar cell, as they provide shunts ruining the device operation. Particularly, the presence of copper selenide segregated at the top surface of the absorber film prior to the deposition of the buffer layer by a chemical bath has been shown to result in the formation of an improper Cu-S buffer, with detrimental effects on the electronics of the device, constituting an additional argument to those reported in the literature for the chemical treatment of surfaces of Cu-rich  $\text{CuGaSe}_2$  films.

Molybdenum diselenide is formed as an interfacial layer during the growth of  $\text{CuGaSe}_2$  on Mo-coated glass substrates, which provide the substrate and the rear contact in standard device processing. This chalcogenide layer develops simultaneously during the chalcopyrite film growth. Its final thickness and structural properties have been shown to depend on a number of factors, including the sodium content of the glass substrate, the gas composition during processing and the substrate conditioning. This layer has been proposed to mediate the electronic rear contact in final devices, regarding the appearance of a blocking behaviour in current-voltage characteristics at low temperatures. The structural characterisation of this layered compound has additionally revealed a characteristic morphology, suggesting a new approach to the lift-off process, by which the active  $\text{CuGaSe}_2$  layers grown on Mo-coated glass can be transferred to alternative substrates with desired properties (e.g. flexibility, or lightness). The feasibility of this approach has been evaluated by means of surface sensitive techniques, demonstrating the absence of Mo remnants on the  $\text{CuGaSe}_2$  rear surface after lifting the film off from the primary substrate. Preliminary results on devices processed on flexible substrates have been presented and their main limiting factors identified, namely the large impact of leakage currents through shunts related to the scribing process for cell isolation.

For the first time, results on the characterisation of the rear surface of  $\text{CuGaSe}_2$  thin films have been presented. The analysis of potential barriers at CGSe grain boundaries have led to estimations of the CGSe net doping concentration ( $2.4 \cdot 10^{16} \text{ cm}^{-3}$ ) and of the density of interface states associated to grain boundaries ( $2.4 \cdot 10^{11} \text{ cm}^{-2}$ ) in good agreement with previous results. Furthermore, comparable values of the work function have been obtained from measurements performed on free surfaces prepared under inert conditions and those measurements carried out on sample cross-sections subjected to a sputtering-cleaning processes in UHV. The suitability of such cleaning process on samples exposed to air, based on short and soft sputtering/annealing cycles, has been assessed, concluding that it provides a convenient sample conditioning prior to KPFM measurements.

CVD-processing on Cu-precursors has been analysed as a potential alternative for the growth of  $\text{CuGaSe}_2$  absorber films. The main advantages of this approach are the provision of closed films showing Cu-rich compositions and the possibility of downscaling the total deposition time, due to an enhanced growth rate compared to standard processing on Mo-coated glass substrates. However, the electronic characterisation of related devices has demonstrated the large impact of leakage currents and a limited range of diode-controlled electronic transport on the device performance.

Further optimisation is thus required for establishing the use of Cu-precursors as an alternative for the open-tube CVD processing.

The most significant improvement in PV performance of devices based on CVD-grown CuGaSe<sub>2</sub> has been recorded on the basis of a modified sequential deposition process. Similar processes have been successfully applied for the growth of Cu-containing chalcopyrites based on co-evaporation techniques. This approach, adapted for CVD, takes advantage of the operational flexibility of the open-tube system, which allows to modify the composition of the gaseous phase determining the film properties during a single process. The two-stage process consists of a nearly stoichiometric first step followed by a Ga- and Se-enrichment stage. As a result, polycrystalline samples combining the preferred morphology of slightly Cu-rich compositions together with the optimal electronic quality of slightly Ga-rich films can be processed. A relative increase of nearly 60 % in efficiency figures of two-stage based devices has been recorded, compared to the top performance of those based on single stage processing, with state-of-the-art solar cells yielding 7.2 % energy conversion efficiencies under standard AM1.5G illumination conditions. This improvement in efficiency is the result of higher short-circuit current densities (up to 14.2 mA/cm<sup>2</sup>) and fill factor figures above 0.6, related to an enlargement of the effective diffusion length of photogenerated minority carriers in the absorber region up to 1.1 μm, compared to the case of single-stage based devices and those processed from Cu-precursors, as determined from comparative studies of quantum efficiency and EBIC measurements. The analysis of the current-voltage characteristics of solar cells as a function of the temperature and illumination, combined with TEM and XPS/UPS studies on the active p-n junction of the devices, have revealed the role of interface recombination as the main limiting factor of CVD-grown CuGaSe<sub>2</sub>-based devices, accounting for the limited open-circuit voltages obtainable.

CVD-grown CuGaSe<sub>2</sub>-based devices are thus not limited by poor bulk properties resulting from the absorber deposition method. Indeed, the results of this study indicate that this technique is a suitable candidate for the growth of CuGaSe<sub>2</sub> films for high-efficiency devices, showing inherent advantages compared to conventional co-evaporation methods (e.g. it does not require high vacuum processing conditions and the source temperature during the deposition process is nearly halved). The success of this approach in the realisation of high-efficiency devices will ultimately depend on the optimisation of those issues related to the formation of the active p-n junction. This may in turn follow from the implementation of pre-treatments for the absorber top surface and the optimisation of the chemical bath recipe for the deposition of the CdS buffer layer, in a similar fashion as it has been reported for PVD grown absorbers. Additionally, the development of the lift-off process based on the simultaneous growth of the interfacial chalcogenide layer should deserve future efforts, as it promises a great potential for eventual tandem-cell implementation and for the use of alternative substrates that may be attractive for product commercialisation. In this respect, efforts should focus on the optimisation of the final steps of device processing, particularly in cell scribing, or alternatively to up-scale the lift-off areas on large substrates and test the implementation of mini-modules. Attending industry requirements for large scale PV production will constitute one of the major added values of CVD-based approaches.

