

Introduction

Photovoltaics (PV) provides a meaningful way for electricity generation. Such statement has been constantly repeated, with increasing volume, by scientist, social groups and consumers over the last decades, as ecological concerns, economic crisis and the unjust richness distribution over the world have become universal issues. When considering the fact that two of the largest PV manufacturers nowadays belong to large oil enterprises, it is not a striking fact that the statement above has begun to be heard also from governments and business men. Indeed, there is little doubt today about the potential of PV as a reliable and clean energy source for terrestrial applications at different levels, ranging from stand-alone systems to large scale plants connected to the grid, as well as of the positive impact this technology has in developing countries. However, these are presumably not the only reasons behind the incorporation of new voices to choir of PV supporters, and additional arguments can be found in recent studies¹ reviewing the situation of PV in the global scenario: in the year 2001, the PV market amounted to nearly 400 MW, showing a steady growth rate of nearly 35 % per annum during the last years with similar previsions for the next decade, which are clearly attractive figures for any conventional product. Regarding the above mentioned potentials of PV, these figures are however still insufficient, far from constituting a noticeable contribution to the world energy consumption, when one is aware that about 2 billion people do not have access to electricity today.

One of the main issues impeding a wider market penetration of PV is the high investment costs associated. Although significant cost reductions by nearly 70 % were already recorded in the decade between 1980 and 1990², PV electricity remains clearly above conventional sources in price in grid connected applications. Subsidising programs at national and regional levels have helped in the last years in the promotion of PV³, with special mention to the 100000 PV-roof program in Germany and the ambitious Sunshine project in Japan. Conventional PV technology, based on silicon wafers, shows however limited room for reducing manufacturing costs, and over the last 15 years increasing interest has been dedicated to the development of a second generation of solar cells⁴. Regardless of the semiconductor material employed, second-generation devices, based on thin-film technology, offer major advantages, including the reduction of material costs by the use of effective absorbers of a few microns thickness, and the increase in the size of the manufacturing unit, from a wafer surface of $\sim 100 \text{ cm}^2$ to that of a glass sheet $\sim 1 \text{ m}^2$. Efforts have been devoted to bringing these devices to competitive figures, comparable to those obtained from silicon-based technology, with impressive results in the last years^{5,6}.

Thin-film solar cells based on I-III-VI₂ chalcopyrite absorbers currently lead the top ranking of energy conversion efficiency in laboratory scale, with 18.8 %⁷. This rapid advance has based on an effective “know how”, not always necessarily linked to a “know why”, in the different steps of device processing⁸. One of the main features of chalcopyrite-based devices, also common to other thin-film technologies, is the large number of compounds and the complexity of the associated heterostructures. As an

example, a typical $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ solar cell without anti-reflecting coating consists of the stacked layer sequence glass/Mo/Cu(In,Ga)(S,Se)₂/CdS/i-ZnO/Ga-Al:ZnO/Ni-Al, which put in words reads: a substrate, a rear contact, an absorber film, a buffer layer, a double window layer and a front contact. It thus follows that the optimisation of such structures is not a trivial problem. Nevertheless, not only small devices of this type show outstanding performance, but also modules from industrial pilot lines show respectable figures close to 13 %⁹.

The critical issue of device performance in chalcopyrite based solar cells still lies largely on the quality of the photoactive absorber layer. When considering a production scale, this aspect is assumed as a trade-off between a satisfactory performance of final devices and both low manufacturing cost and a large throughput. Thus, the search and assessment of feasible alternatives to cost-inefficient growth methods, though providing excellent material quality in laboratory scale, are fields of increasing interest. Regarding the materials science involved in chalcopyrite thin-film PV, a continuous progress in the understanding of the properties of these compounds has been achieved over the last decade, narrowing the gap between those outstanding results based on empirical knowledge and the comparatively poor background on the fundamental electronic and structural processes taking place in the device fabrication and operation. Alloying ternary compounds, CuInSe_2 , CuInS_2 , CuGaSe_2 and CuGaS_2 in quaternary and pentanary compounds like $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$, offers the possibility of adjusting the absorber band gap between 1 eV up to 2.4 eV, thus in the range of interest for PV applications. Currently, the highest efficiency figures are achieved with materials of low band gap ~ 1.2 eV, but the possibility of designing devices yielding high output voltages, is driving the attention towards wide gap partners.

In this sense, CuGaSe_2 shows interesting properties for PV applications. With a wide band gap of 1.7 eV, well matched with the solar spectrum, and a high absorption coefficient, this direct semiconductor promises high output voltages, low efficiency losses related to high temperature operation and low resistive losses in module implementation. Furthermore, the combination of CuGaSe_2 and CuInSe_2 in a tandem device, in which each device partner absorbs in different ranges of the solar spectrum, has been theoretically calculated to yield energy conversion efficiencies close to 40 %. However, the degree of fundamental knowledge and of device development of CuGaSe_2 lag well behind those of related chalcopyrite compounds, like CuInSe_2 , CuInS_2 and the alloys $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$. Basic research on CuGaSe_2 is thus still required prior to facing the challenge of tandem device implementation and module fabrication.

In this work, the chemical vapour deposition (CVD) approach to the growth of polycrystalline CuGaSe_2 thin-films for PV applications will be assessed. This method offers attractive advantages compared to conventional alternative systems, like those based on co-evaporation, as it operates at moderate source temperatures (600°C) and it relaxes the requirement of processing under high vacuum conditions. Furthermore, the system employed, a modified CVD set-up developed at the Hahn-Meitner-Institut, consisting of an open-tube reactor and using two different loads of binary compounds Cu_2Se and Ga_2Se_3 as source materials, provides a flexible control on the deposition process. The study, organised as follows, comprises the microstructural and electronic characterisation of CVD-grown CuGaSe_2 films and related devices, with the aim of evaluating the suitability of the absorber deposition method for PV applications.

Chapter 1 provides a general overview of the material properties and the key issues directly related to the application of CuGaSe₂ in PV devices. The basics of solar cell operation are presented, with special attention to the description of those models and parameter relationships required for the interpretation of the experimental results later on. A brief revision of the chalcopyrite thin-film technology, including the description of the different steps involved in device processing, closes the chapter.

In Chapter 2, the various characterisation techniques used in this work for the study of CuGaSe₂ films and related devices are briefly reviewed, providing the reader with the fundamental physical concepts behind them and a short description of the experimental set-ups. The chapter is divided in three sections, beginning with those tools used for the compositional and structural characterisation, which include scanning and transmission electron microscopies (SEM and TEM), energy-dispersive X-ray analysis (EDX), X-ray diffraction (XRD), X-ray fluorescence (XRF) and photoelectron emission spectroscopies (XPS and UPS). In Section 2.2 the tools used for the electronic characterisation of devices will be introduced, including the electron-beam-induced current method (EBIC), the analysis of current-voltage characteristics (I-V) and the quantum efficiency (QE). Section 2.3 introduces the Kelvin probe force microscope, which due to its special characteristics, is considered as a bridge between structural and electronic characterisation methods.

Chapter 3 starts with a description of the open-tube CVD deposition system used in this work for the growth of the CuGaSe₂ absorber films. Results on the system operation will be presented, highlighting those aspects related to limiting factors in film quality and the optimisation of the deposition process. Special attention is paid to the film properties as a function of their composition, as this aspect turns out to be crucial for the subsequent device operation. Particularly, the appearance of secondary phases, namely copper selenides and molybdenum diselenide, and their properties are extensively analysed. Based on this study, new approaches to the optimisation of the absorber deposition process are presented and evaluated, which include the implementation of sequential depositions and the use of Cu-precursors.

In Chapter 4 the electronic characterisation of CuGaSe₂ devices is presented. The chapter begins with a study on the formation of the active p-n junction governing the state-of-the-art device operation, which will be combined with microstructural aspects of the interfacial region. The subsequent electronic characterisation of complete solar cells evaluates in a comparative study the performance of devices based on the various deposition approaches introduced in the previous chapter. Results of the electronic characterisation will be related to those aspects of the microstructural analysis presented previously. In particular, the impact of interfaces involving the absorber film on the device electronics will be monitored, in relation to the prominent role of interface recombination of photogenerated charge carriers at the absorber/buffer junction, and with the appearance of a blocking behaviour in the current-voltage characteristics of devices operated at low temperatures. A new model for the latter phenomenon will be presented and assessed, which includes the mediation of an interfacial molybdenum diselenide layer identified in Chapter 3 at the rear contact.

Also in connection with the interfacial molybdenum diselenide layer, a new approach to the so-called lift-off technology is presented in Chapter 5. This method, based on the transfer of active thin-films from conventional to alternative substrates, is gaining interest in the PV field, as it widens the potential applications of solar cells in consumer

products and promises manufacturing cost reduction with cheap substrates. The microstructural analysis carried out in Chapter 3 on the interfacial chalcogenide layer suggests a lift-off procedure for CuGaSe₂ thin-films grown by CVD on standard Mo-coated glass substrates that is stated and evaluated in this chapter. The crucial aspect of the lifted-off surface cleanness will be analysed, showing for the first time results on the microstructure and electronics of the rear surface of CuGaSe₂ films, and demonstrating that the suggested lift-off approach provides active chalcopyrite surfaces with no remnants of MoSe₂ on it, being thus suitable for further device processing. Preliminary results on the characterisation of devices based on lift-off absorbers on flexible substrates will be presented, together with the main factors found to limit their performance.

In Chapter 6 the main results of this work will be summarised, closing with some remarks on the potential of CVD-based techniques for the fabrication of high-efficiency devices and prospects for the further development of the lift-off process presented in Chapter 5.