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Hybrid sputtering/evaporation deposition of Cu(In,Ga)Se_2 thin film solar cells

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Abstract

In this work, an alternative approach for CIGS thin film growth has been tested, which is different from the common co-evaporation process. Such approach consists of sputtering deposition of the metal elements combined with selenium evaporation. This new and easily scalable procedure allows deposition time of the CIGS layer lower than 15 minutes and can be easily applied not only on rigid but also on flexible substrates in a roll to roll configuration, matching industrial application requirements. The relationships between the growth parameters of such hybrid sputtering/evaporation method and the chemical-physical properties of the CIGS films and cells have been studied.

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Keywords: CIGS; sputtering; thin film solar cells; photoluminescence; recombination

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1. Introduction

In the last decades, the run-up in both the fossil fuel prices and the related global warming turned the attention towards environmentally clean alternative energy resources. Among them, photovoltaics (PV) is a reliable choice to meet the global energy demand. However, despite the many advantages of this unlimited and clean resource, the high cost of manufacturing and installation of first generation silicon based devices hindered a widespread PV commercialization.

The strong need of reducing the PV related cost focused therefore the attention on thin film based devices. Such technology in fact allows improving the efficiency to cost ratio, since the amount of material required for the realization of thin film solar cells is at least two order of magnitude lower than in the case of first generation PV devices. Among these second generation thin film devices the alloy $Cu(In,Ga)Se_2$ (CIGS) is the most promising material due to the high stability and the high efficiencies recently obtained (η=20.1 % lab record) [1]. A further reduction of CIGS solar cells cost could be achieved developing new easily scalable procedures not only on rigid but also on flexible substrates, this feature being really attractive for building integrated (BIPV) systems.

In this work, a new and alternative approach for CIGS thin film growth has been tested, different from the commercial system mainly based on co-evaporation process. Such approach consists of sputtering deposition of the metal elements combined with selenium evaporation, which allows deposition time of the CIGS layer lower than 15 min, matching industrial application requirements. The cylindrical geometry of the deposition chamber can be exploited for a continuous process (roll-to roll approach) and different substrates can be used (11x14 cm^2 soda lime glass, 120x14 cm^2 stainless steel or 120x14 cm^2 polyimide substrates). In this paper only results obtained on glass substrates will be reported even if deposition on stainless steel-foil has already been tested.

Furthermore, considering that the optoelectronic properties of the absorber layers are strongly dependent upon the deposition method, the relationships between the growth parameters and the chemical-physical properties of the CIGS films and the cell parameters have been also studied and are here reported. This approach is essential both for the optimization of the growth process and for a better understanding of the relationship between microstructure and efficiency in such complex material. Further informations about the properties of CIGS solar cells have been achieved by a comparison between measured and simulated I-V characteristics, which provide for important cell parameters, like the presence and the amount of recombination centers.

2. Experimental details

The CIGS absorber layer was deposited by an alternative growth approach based on an sputtering/co-evaporation process for very high-throughput manufacturing patented by Voltasolar SpA (patent N° TO2007A000648). The Cu–In–Ga metallic precursors were prepared by sequential sputtering from In and Cu–Ga (28 at%) alloy targets, respectively, on glass substrates using DC magnetron sputtering system. The metallic precursors were subsequently selenized to form the CIGS films. In the selenization process, solid Se pellets were used as selenium source, using thermal evaporation system.

The deposition chamber used allows cyclically exposing the heated substrate in front of two magnetron sputtering sources and in front of the effusion cell to generate the selenium vapour. During the deposition, the growth parameters like target current, deposition temperature, rotational speed, deposition and selenization time can be controlled and changed by a proper software.

$CuIn_{(1-x)}Ga_xSe$ films with a thickness around 1.5–2.5 μm were obtained. Mo back-contact layer was deposited by DC magnetron sputtering using the same chamber.

The grown CIGS films were characterized by Scanning Electron Microscopy (SEM) for the morphology, by EDX and SIMS for the compositional analyses, photoluminescence for band gap and recombination centers identification and XRD for structural information.

The large 11x14 cm^2 soda lime glass substrates with the Mo and CIGS layers were cut in smaller pieces (5x5 cm^2) for the cell finalization. Solar cells were fabricated using CdS as buffer layer (50-70 nm) deposited by chemical bath deposition (CBD) and ZnO (80-100 nm) + ITO (300 nm) deposited by RF sputtering. Typical resistivity for the ITO films is around $4x10^{-3}$ Ohm cm. Finally, different 0.5 cm^2 solar cells were obtained on these 5x5 cm^2 substrates using a mechanical scribing. The CIGS cell performances have been monitored by External Quantum Efficiency measurements and I-V measurements under AM1.5 conditions.

3. Results and Discussion

XRD data show that the CIGS layers have the expected chalcopyrite phase composition [2]. The element concentration ratios in the grown films provided by EDS are the following: [Ga]/([Ga]+[In]), between 0.20 and 0.25 for all the samples; [Cu]/([In]+[Ga]) between 0.7 and 0.98, i.e. the range required for high efficiency solar cells, as reported in literature [3]. The films present a homogeneous and dense morphology with a columnar structure. The grain diameters are around 0.5 μm.

The optimization of the absorber layers growth procedure has been performed on the basis of the electrical characterization results obtained on the corresponding CIGS solar cells. Starting from the first deposition, a progressive increase of the cell parameters (efficiency, open circuit voltage, short circuit voltage, fill factor) has been observed, as summarized in the efficiency evolution plot reported in Fig. 1.

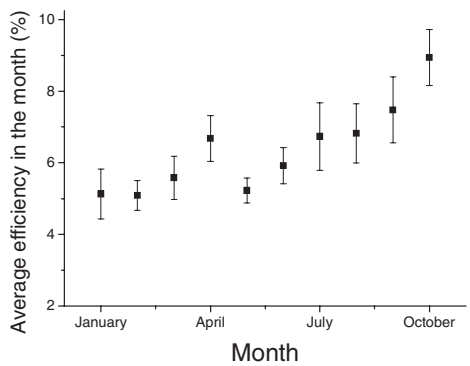

Fig.1. Efficiency evolution for the CIGS cells deposited on glass achieved in 8 months. In the figure the average obtained in the month (around 10 depositions a month) is reported.

The best results so far obtained on cells without antireflection coating are reported in Table 1.

In order to investigate the possible reasons for the low V_{oc} values so far obtained, SCAPS software [4] was used for the simulation of IV curves under solar simulator. The simulation of the cell with the best parameters indicated a high density of recombination centers (around $4x10^{17}$ cm^{-3}). Reducing the density of deep recombination centers by one order of magnitude allows to increase the V_{oc} value from 512.6 mV to 578 mV and the efficiency over 13%, as reported in Fig. 2.

Table 1. Best results obtained with CIGS solar cells on glass substrates

Substrate	Eff (%)	Voc (mV)	Jsc (mA/cm^2)	FF (%)	Area cm^2
Glass	10.1	512.6	30.11	65.43	0.5

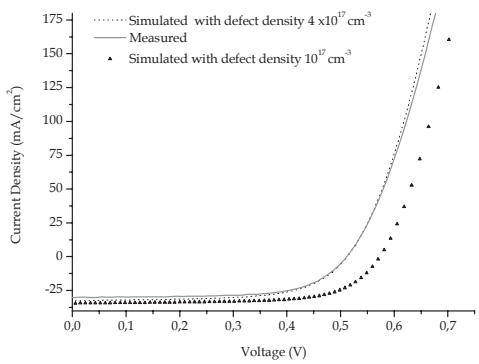

Fig. 2. IV data and SCAPS simulation of the best solar cell so far obtained. A simulated IV curve with a reduced defect density is also reported (triangle)

The presence of recombination centers in our CIGS film is also confirmed by the EQE measurements (see Fig.3). The decrease at higher wavelength are fingerprints of high recombination in the bulk.

PL spectra collected both at room and low temperature, do not shown any radiative deep levels or band tails ascribed to grain boundaries. In the as grown sample the PL spectrum can be fitted with three peaks using a Gaussian distribution (see Fig. 4a). The peak at 1.13 eV is related to a band to band transition and its energy position is in agreement with the band gap value calculated by the semiempirical formula

reported in [5] using the elemental composition of the film. The second peak at 1.1 eV is a free to bound transition from a donor level related to V_{Se} (whose ionization energy is around 50 meV) to the valence band. The third peak at 1.07 eV is related to a free to bound transition from the conduction band to an acceptor level (maybe $2V_{Cu}^{-} + In_{Cu}^{2+}$ with ionization energy around 0.1 eV).

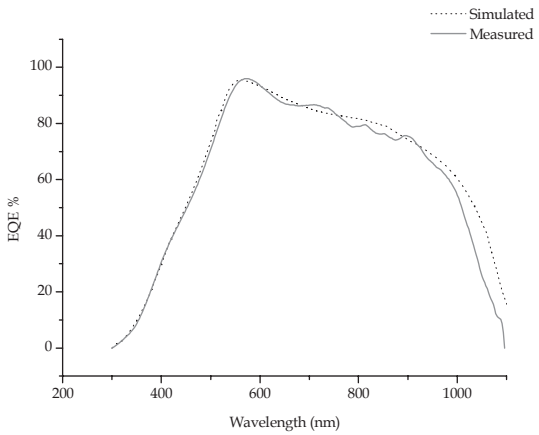

Fig. 3. Typical EQE measurement for CIGS solar cells fabricated in this work. The simulated EQE curve with SCAPS program with a defect density 4 x 10 ^{17} cm^{-3} is also reported (dot lines).

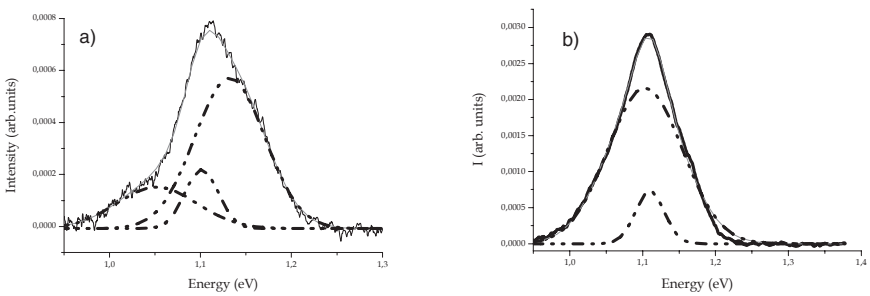

Fig. 4. PL spectra fitting by Gaussian curves (dotted lines): a) as grown CIGS film, b) CIGS solar cell

The PL spectrum collected on the CIGS solar cell shows instead intensity several times higher than the starting material and besides the peak related to band to band transition shows only the free to bound peak at 1.1 (Fig. 4b). Such modification in shape and intensity between the two spectra can be ascribed to the passivation of levels associated to V_{Cu} by Cd during the buffer layer deposition in the Cu-poor surface of the CIGS absorber layer, in agreement with [6].

4. Conclusions

Efficient small-area CIGS cells with 10% efficiency were fabricated with an innovative hybrid sputtering system. Even if it is known that CGIS solar cell clearly exceeding 10% efficiency have been

obtained worldwide on glass substrate, this is a very encouraging result considering the relative small time spent on such research activity (8 months) and the potentiality and the advantages of this technique. This method is suitable for economic and large-scale manufacture since it allows deposition time less than 15 min and can work in a roll to roll scheme on flexible substrate. Furthermore, the results of optoelectronic characterization and IV simulations indicate that the not yet optimal Voc values so far obtained are ascribed to the presence of deep levels, most probably related to extended defects like precipitates of spurious phases. Further analyses (XRD and EXAFS measurements) on this topic are underway.

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